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CATALYTIC DEHYDROGENATION OF LIQUID ORGANIC HYDROGEN CARRIERS

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Chemical Engineering

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 14th of September, 2018.

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Abstract of master's thesis

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Abstract

Liquid organic hydrogen carriers (LOHCs) provide a novel method for storing hydrogen. Hydrogen is chemically bound to a carrier compound, which means that hydrogen is not in its flammable form and in addition, no boil-off occurs. Because of this, storage in LOHCs is safer and more efficient, compared to conventional storage methods.

The main focus of the literature part is in presenting and comparing different reactor concepts for LOHC research and commercial applications. It was found, that micro-structured reactors or heat exchanger reactors could be the most optimal reactor concepts for LOHC dehydrogenation applications as they offer the best heat and mass transfer of all studied reactor concepts. Currently, only one commercial LOHC unit exists. The most commonly used and most researched LOHC compounds are dibenzyltoluene, N-ethyl-carbazole and methylcyclohexane. The environmental hazards of LOHC compounds are related to their decomposition products, e.g. benzene.

The experimental part of this thesis covers the dehydrogenation of perhydro-dibenzyltoluene on different platinum catalysts. The tested catalysts were Pt/Al_2O_3 in packed bed and washcoat form, Pt/TiO_2 in washcoat form and Pt/C in packed bed form. The experiments were carried out on different temperatures (270 - 300 °C) and space velocities to compare how the catalysts perform at different conditions. In addition, longer, 48h experiments were carried out to observe catalyst behavior during longer continuous operation. In general, the degree of dehydrogenation (conversion) was higher at lower space velocities (longer residence time) and higher temperatures. The degree of decomposition was observed to be proportional to the degree of dehydrogenation. Washcoat catalysts generally yielded lower degree of decomposition than packed bed catalysts.

Of the studied catalysts, Pt/TiO_2 was found to be the best dehydrogenation catalyst as it yielded the highest degree of dehydrogenation and lowest degree of decomposition at typical dehydrogenation conditions. At 300 °C with weight hourly space velocity of 4.57 h^{-1} the degree of dehydrogenation was 39 % and degree of decomposition was 0.7 %. Based on the experimental results and the literature review, a micro-structured reactor or a heat exchanger reactor with multiple narrow tubes washcoated with Pt/TiO_2 would be a viable rector concept for commercial LOHC dehydrogenation applications.

Keywords dehydrogenation, liquid organic hydrogen carrier, platinum catalyst, hydrogen

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Tiivistelmä
Nestemäiset orgaaniset vedynkantajat tarjoavat uuden menetelmän vedyn varastoimiseksi. Tässä menetelmässä vety on kemiallisesti sidottu kantaja-aineeseen, jolloin vetyä ei lainkaan esiinny sen helposti syttyvässä muodossa. Vedyn spontaania vapautumista ei myöskään tapahdu. Tästä syystä tämä menetelmä tarjoaa turvallisemman ja tehokkaamman tavan varastoida vetyä kuin perinteisesti käytetyt menetelmät.

Kirjallisuusosa keskittyy pääosin erilaisten vedyn kantaja-aineiden tutkimuksessa ja mahdollisissa kaupallisissa sovelluksissa käytettyjen reaktorikonseptien esittelyyn ja vertailuun. Kirjallisuuden perusteella voidaan todeta, että mikrorakenteiset reaktorit ja lämmönvaihdinreaktorit sopivat parhaiten vedynkantajien vedynpoistosovelluksiin niiden erinomaisten lämmön- ja aineensiirto-ominaisuuksien takia.

Diplomityön kokeellisessa osassa poistettiin vetyä perhydro-dibenzyltolueenia erilaisilla platinakatalyyteillä. Testattuja katalyyttejä olivat Pt/Al_2O_3 pakattuna petinä ja pintakerroksena, Pt/TiO_2 pintakerroksena ja Pt/C pakattuna petinä. Kokeita suoritettiin eri lämpötiloissa (270 - 300 °C) ja vaihtumissa, jotta voitiin verrata katalyyttien toimintaa eri olosuhteissa. Lisäksi tehtiin pidempiä 48 tunnin kokeita, jotta voitiin selvittää, miten katalyytit käyttäytyvät pidemmän yhtäjaksoisen käytön aikana. Havaittiin, että vedynpoistosaste (konversio) oli suurempi pienemmillä vaihtumilla (pidempi viipymäaika) ja korkeammissa lämpötiloissa. Lähtöaineen hajoamisasteen havaittiin myös olevan suoraan verrannollinen vedynpoistoasteeseen. Pintakerroskatalyyteillä hajoamisaste oli alhaisempi kuin pakatuilla pedeillä.

Tutkituista katalyyteistä Pt/TiO_2:n havaittiin olevan paras vedynpoistokatalyytti, koska se tuotti korkeimman vedynpoistoasteen ja pienimmän hajoamisasteen tyypillisissä reaktio-olosuhteissa. Massavaihtumalla 4.57 h^{-1} ja 300 °C:ssa vedynpoistoaste oli 39 % ja hajoamisaste 0.7 %. Tulosten perusteella mikrorakenteiset reaktorit tai kapeaputkiset lämmönvaihdin reaktorit Pt/TiO_2 pintakerroskatalyytillä ovat sopivia kaupallisiin vedynkantajien vedynpoistosovelluksiin.

Avainsanat dehydrogenointi, nestemäiset orgaaniset vedynkantajat, platinakatalyytit, vety

Foreword

This master's thesis was carried out at VTT Technical Research Centre of Finland in the Catalyst Technology team. The thesis was part of the LOHCNESS project (http://www.vtt.fi/sites/lohcness) and was completed between the February and August of 2018.

I thank Pekka Simell for giving me the opportunity to complete my master's thesis at VTT on such an interesting topic. I also present my thanks to my supervisor, Professor Riikka Puurunen, and advisor D.Sc (Tech) Noora Kaisalo for their skillful guidance and feedback. Special thanks go to Mari-Leena Koskinen-Soivi and Katja Heiskanen for all their help with my lab work. I also thank Niko Heikkinen, Matti Reinikainen, Petri Hietula, Laura Keskiväli and Päivi Aakko-Saksa from VTT and You Wayne Cheah from Aalto University for their help with different aspects of the experimental work.

Finally, I want to thank my family and friends for their continuous support during my work on this thesis.

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Abbreviations

BT	Benzyltoluene
CMR	Catalytic membrane reactor
DBT	Dibenzyltoluene
dodc	Degree of decomposition
dodh	Degree of dehydrogenation
doh	Degree of hydrogenation
H12-BT	Perhydro-benzyltoluene
H18-DBT	Perhydro-dibenzyltoluene
H12-NEC	Perhydro-N-ethylcarbazole
LHSV	Liquid hourly space velocity
LOHC	Liquid organic hydrogen carrier
MCH	Methylcyclohexane
NEC	N-Ethylcarbazole
PEM	Proton exchange membrane
QSAR	Quantitative Structure-Activity Relationship
SMR	Staged membrane reactor
WHSV	Weight hourly space velocity

Symbols

A_{dec}	Sum of the areas of decomposition mass spectra peaks
A_i	Area of the compound i's mass spectra peak
A_{total}	Sum of the area of all product peaks (main products + decomposition products)
b	Intercept of the calibration curve
$\mathrm{dodc}_{product}$	Degree of decomposition of the product
$\mathrm{dodc}_{reactant}$	Degree of decomposition of the reactant
$\mathrm{dodc}_{\mathrm{total}}$	Total degree of decomposition
F_{i,H_2}	Hydrogen flow in to the reactor
$F_{i,tot}$	Total raw material flow in to the reactor (ml/min)
k	Slope of the calibration curve
$K_{o/w}$	n-Octanol/Water Partition Coefficient
M	Molecular weight of the compound (g/mol)
m_{cat}	Mass of the catalyst (g)
$\dot{m}_{H_2}$	Mass flow of hydrogen
m_{in}	Mass flow in to the reactor (g/h)
$\dot{n}_{H_2}$	Molar flow of hydrogen (mol/min)
p	Ambient pressure (Pa)
R	Ideal gas constant, 8314000 $\frac{cm^3 \cdot Pa}{K \cdot mol}$
T	Ambient temperature (K)
$V(\%)$	Percentage value reading of the flow controller
V_{cat}	Volume of the catalyst (ml)
$\dot{V}_{H_2}$	Volume flow of hydrogen (ml/min)
$\dot{V}_{in}$	Liquid flow in to the reactor (ml/h)
w_{H_2}	Hydrogen weight capacity for the LOHC compound
$x_{H18-DBT}$	Amount of LOHC in the raw material (purity)
x_i	Relative amount of decomposition product i
X_i	Total isomer peak fraction area / Total fractions peaks area

1. Introduction

Due to climate change and the environmental problems caused by it, more and more emphasis has been put on the development of energy production from renewable energy sources such as wind and solar power. However, the production and consumption of renewable energy do not always coincide. They may vary in terms of timing and region. There are times of over-production on very windy or sunny days and energy shortages during unfavorable seasons [1]. To stabilize these fluctuations, new energy storage methods have to be developed so that the excess energy produced can be stored and used during times of lower energy production.

One proposed method is to use the excess energy to produce hydrogen by water electrolysis, thus storing the energy chemically as hydrogen [2]. Conventionally, hydrogen has been stored either in liquid form or as a compressed gas. These forms of energy storage are problematic as the hydrogen is in its highly flammable molecular form, which makes handling it difficult and requires special storage units. This can be avoided by using a novel way to store hydrogen by chemically binding it to a carrier compound. These compounds are called liquid organic hydrogen carriers (LOHCs). They offer a new and safer way to store hydrogen as no molecular hydrogen is present in them. The carrier compounds are diesel-like organic compounds, which are relatively easy to handle and can utilize the existing storage and transport infrastructure. Furthermore, no boil-off or other unwanted release of hydrogen is experienced with LOHCs [3], making them safe for long-term storage. Compared to the conventional storage methods, LOHCs also have higher hydrogen storage capacity. Schneider et al. [3] compared the capacities of LOHCs to conventional hydrogen storage methods. In the conventional compressed gas storage of hydrogen at 300 bar pressure, a storage for 3 kg of hydrogen requires a volume of over 150 liters. When bound to LOHCs, the required volume for the same amount of hydrogen is just under 53 liters. This allows for more efficient transportation and storage of hydrogen, reducing the storage and transport costs significantly.

The main focus of the literature part of this thesis is the review and comparison of different viable reactor concepts for LOHC dehydrogenation. In the literature part, also an overview of the LOHC technology and its current state is presented.

The aim of the experimental part was to find the most suitable dehydrogenation catalyst for perhydro-dibenzyltoluene (H18-DBT). In addition, packed bed and washcoated catalysts were compared to determine, which application would be more suitable for scale up experiments and commercial applications. To achieve the goals of the thesis, the dehydrogenation of perhydro-dibenzyltoluene was studied on different platinum catalysts at different conditions. In total, three different catalyst were tested: Pt/Al_2O_3, Pt/TiO_2 and Pt/C. Of these three, Pt/Al_2O_3 was tested in packed bed and washcoated form whereas Pt/TiO_2 was tested in washcoat form and Pt/C as a packed bed. In the experiments, different space velocities and temperatures were tested. In addition, longer, 48-hour experiments were carried out to study the behavior of the catalysts during continuous operation. Based on the literature review and the experiment results, recommendations are given for future research, reactor concepts and commercial applications.

2. Liquid organic hydrogen carrier system

2.1 Working principle

Energy storage via the liquid organic hydrogen carrier (LOHC) system is based on the hydrogenation and dehydrogenation of a liquid organic carrier. First, the hydrogen is chemically bound to the liquid carrier. There is no molecular hydrogen present at this stage, which makes the storage and transport of the carrier safe [3]. The liquid carrier is then transported to a location where it can be distributed further, e.g. a fuel station or another energy storage site. There, the carrier is later catalytically dehydrogenated to release the hydrogen for energy use when needed. The hydrogen can be transformed into energy with, for example, proton exchange membrane (PEM) fuel cells [4]. The hydrogen depleted carrier is then recycled back to the hydrogenation site and hydrogenated again to repeat the cycle.

The hydrogenation of the carrier is an exothermic reaction and the dehydrogenation is an endothermic reaction. The heat released by the exothermic reaction and the heat demand of the endothermic reaction are identical and dependent on the carrier compound. The enthalpy varies between 50.6 kJ/mol H_2 and 72 kJ/mol H_2 for some of the most common carriers [3], [5]. The reaction conditions also vary for different compounds, but in general the dehydrogenation of the carrier is performed at lower pressures (approx. 1 atm) and higher temperatures (270–350 °C), depending on the reactor and the LOHC compound used [3], [5]–[7]. The hydrogenation is carried out at higher pressures of 50–70 bar and lower temperatures of 100–250 °C [2], [3], [5]. The reactions are usually carried out on noble metal catalysts. For example, Ru and Pt on Al_2O_3 support can be used for the hydrogenation and dehydrogenation of the liquid organic hydrogen carriers [2]. The hydrogenation and dehydrogenation take place gradually. For example, in the case of dibenzyltoluene (H0-DBT) and its hydrogenated form perhydro-dibenzyltoluene (H18-DBT), the hydrogenation and dehydrogenation happens in steps from H0-DBT to H6-DBT to H12-DBT and finally to H18-DBT and vice versa [8].

2.2 Liquid organic hydrogen carriers

Liquid organic hydrogen carriers (LOHCs) are organic compounds which have the ability to store large quantities of hydrogen, i.e. they have many double bonds, which can be hydrogenated. The amount of hydrogen that can be bound to these compounds is typically between 3.0-10.8 wt-% [5]. Bourane et al. [5] have listed some characteristics for good LOHCs: low enthalpy of dehydrogenation, low volatility, low toxicity, small environmental impact, low cost, reversibility of the reaction without significant degradation, liquid state at all stages of the operation and high weight and volume storage densities of hydrogen. The compounds reported in the literature include cycloalkanes [7], polycyclic alkanes [9], heteroatom containing hydrocarbons [9][10] and ionic liquids [11]. Here, four of the most promising and most studied carrier compounds are presented: benzyltoluene, dibenzyltoluene, N-ethylcarbazole and methylcyclohexane. The properties of these LOHC compounds are shown in Table 1.

Table 1. Properties of BT, DBT, NEC and MCH. [2], [5]

	BT	DBT	NEC	MCH
Melting point (°C)	-30	-36	68	-126
Boiling point (°C)	280	390	270	101
H2 capacity wt-%	6.2	6.2	5.8/5.2	6.1
Enthalpy of hydrogenation/ dehydrogenation (kJ/mol)	71	71	55	68.3

2.2.1 Benzyltoluene and dibenzyltoluene

Benzyltoluene (BT) and dibenzyltoluene (DBT) are conventionally used as heat-transfer fluids in industrial applications under tradenames Marlotherm LH and Marlotherm SH, respectively. Both are well studied compounds with good availability and low cost. [2]. Their structures are presented in Figure 1.

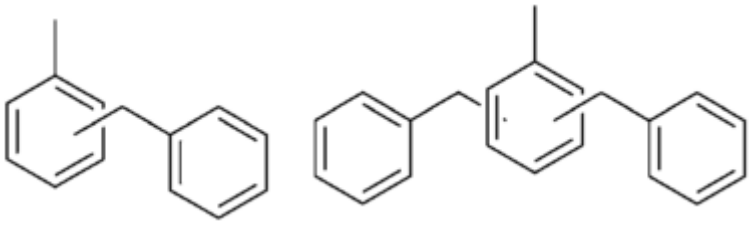

Figure 1. Structures of benzyltoluene (left) and dibenzyltoluene. Reproduced from [2].

Both BT and DBT have a hydrogen weight capacity of 6.2 wt-% [2]. Twelve hydrogen atoms can be bound to the BT and eighteen to the DBT. The structures of perhydro-benzyltoluene (H12-BT) and perhydro-dibenzyltoluene (H18-DBT) are presented in Figure 2.

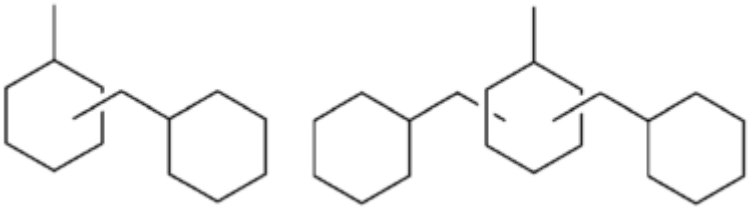

Figure 2. Structures of perhydro-benzyltoluene (left) and perhydro-dibenzyltoluene. Reproduced from [2].

The heat released by hydrogenation of BT and DBT is 71 kJ/mol H_2, which is the same as the heat demand of dehydrogenation for H12-BT and H18-DBT. Both hydrogen lean forms of the compounds are liquid in ambient conditions with melting points of -30 °C for BT and from -36 °C for DBT. The boiling points of the substances are 280 °C and 390 °C, respectively, both of which are over the normal dehydrogenation temperatures of these compounds [2], [12], [13]. The physical properties (density, viscosity, surface tension, boiling point, etc.) of BT are similar to diesel, which makes it easy to handle and transport [12]. DBT is also similar to diesel, with the exception of viscosity, which is approximately an order of magnitude higher than diesel's, making the handling of DBT slightly more difficult [13]. Nevertheless, existing infrastructure can be used to store and transport both of these carrier compounds [3]. These compounds also show good stability during dehydrogenation yielding less than 0.01 % of decomposition products during 72 h under typical dehydrogenation operation conditions [2]. The

amount of decomposition products increases with increasing conversion (degree of dehydrogenation) of the compounds. However, the degree of decomposition is only 0.2 % even under complete dehydrogenation. The main decomposition products are methane, toluene, benzene, methylcyclohexane and cyclohexane [4].

Differences between the two compounds can be found in the times required for hydrogenation and dehydrogenation [2]. Benzyltoluene is a smaller compound and thus will not have as high pore-diffusion limitations in the catalyst particles as dibenzyltoluene. As a result, BT requires less time to undergo full hydrogenation to the H12-BT form. Similarly, H12-BT requires less time to reach any degree of dehydrogenation than H18-DBT.In addition, due to BT being a smaller compound than DBT, its viscosity is also smaller and thus its application and handling is easier. However, dibenzyltoluene has an order of magnitude lower vapor pressure at the typical dehydrogenation conditions compared to benzyltoluene, making it more stable, and thus more suitable as a carrier material [12]–[14]. Both carrier compounds are environmentally hazardous, but BT is also irritant, which makes it less safe to handle [15], [16]. The recent publications about benzyltoluene derivatives have concentrated solely on dibenzyltoluene instead of benzyltoluene [4], [17]–[20].

2.2.2 N-ethylcarbazole

Another well studied LOHC compound pair is N-ethylcarbazole (NEC) and its hydrogenated form perhydro-N-ethylcarbazole (H12-NEC). Their properties and applications for LOHC technology have been studied by e.g. Pez et al. [9] and Jiang et al. [10]. The structures of NEC and H12-NEC are presented in Figure 3.

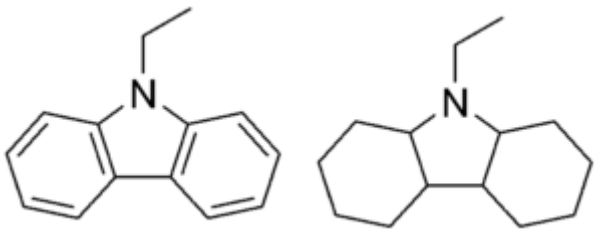

Figure 3. Structures of N-ethylcarbazole (left) and perhydro-N-ethylcarbazole. Reproduced from [2]

Compared to benzyltoluene and dibenzyltoluene, NEC has lower enthalpy of dehydrogenation (55 kJ/mol compared to 71 kJ/mol). This denotes that the dehydrogenation of the NEC has a more favorable thermodynamic driving force, indicating that the dehydrogenation can be carried out at lower temperatures [2]. It has been found, that the lower enthalpy is caused by the replacement of a carbon atom with a heteroatom, here nitrogen [9]. The more favorable thermodynamics of NEC in LOHC dehydrogenation can be seen in the experiments carried out by Brückner et al. [2]. In their experiment, dehydrogenation of DBT required 80 °C higher temperature to reach the same degree of H_2 release (95 %) as NEC when the most suitable catalyst system was applied to each substrate. Compared to the benzyltoluene derivatives, NEC also has slightly lower hydrogen capacity (5.8 wt-% vs 6.2 wt-%) and boiling point (270 °C vs 280/390 °C) [2].

Major drawbacks of NEC compared to BT and DBT are its limited availability, higher melting point (68 °C vs -30/-36 °C) and lesser thermal stability at higher temperatures e.g. 270 °C [2]. Most of the NEC is currently produced by coal tar distillation with a global capacity of less than 10 000 t/a [2]. The high melting point means that the compound is in solid state in ambient conditions, which complicates its processing. Finally, the limited thermal stability causes the compound to break down under prolonged heating at 270 °C in the presence of typical dehydrogenation catalyst. After heating for 72 h, the yield of decomposition products is over 1 % [2]. The decomposition happens by dealkylation yielding carbazole and methane [2], [21].

Some of the drawbacks, mainly the high melting point and instability, can be countered or at least alleviated. For instance, even though pure NEC is solid in ambient conditions, it has been found that NEC mixtures with partly dehydrogenated forms of NEC are liquids at ambient temperature [22]. This mixture however decreases the hydrogen capacity of NEC to 5.2 wt-%. In addition, because the enthalpy of dehydrogenation for NEC is lower, the dehydrogenation can be carried out at lower temperatures, where the degree of decomposition is lower, due to the more favorable thermodynamics i.e. lower required thermodynamic driving force [2]. Some dehydrogenation experiments with NEC have been carried out at temperatures between 170 °C and 260 °C [2], [22], [23].

2.2.3 Methylcyclohexane

Methylcyclohexane (MCH) and its corresponding dehydrogenated form, toluene, are another suitable and well-studied compound pair for LOHC applications. Both compounds are liquid in ambient conditions as the melting point of methylcyclohexane and toluene are -126 °C and -93 °C, respectively. The boiling points of the compounds are 101 °C for MCH and 111 °C for toluene. The enthalpy of hydrogenation and dehydrogenation are 68.3 kJ/mol and -68.3 kJ/mol, respectively. Toluene is a common chemical with well-studied properties, good availability and a hydrogen weight capacity of 6.1 wt-% [5]. The structures of methylcyclohexane and toluene are presented in Figure 4.

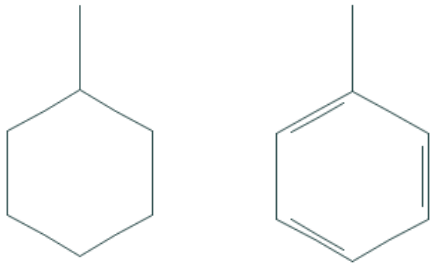

Figure 4. Structures of methylcyclohexane (left) and toluene. Reproduced from [24], [25].

One major drawback of the toluene/MCH system is the low boiling point of the compounds. Due to the low boiling points, both toluene and MCH are gaseous at hydrogenation and dehydrogenation conditions. Because of this, the isolation of pure hydrogen is difficult and requires extensive condensation and purification steps [21]. Another concern for this LOHC compound pair is the low flashpoint of the compounds, which is below the dehydrogenation temperature. Furthermore, due to the high dehydrogenation enthalpy and the resulting high required thermodynamic driving force, high temperatures are required for efficient dehydrogenation [21].

Despite all this, successful experiments have been conducted with methylcyclohexane. Okada et al. [26] carried out an experiment where gaseous methylcyclohexane was continuously pumped through a fixed bed reactor at 320 °C and ambient pressure for 6000 h. During the whole operation, MCH conversion of 95 % remained stable and toluene selectivity was >99.9 %. The main

side products were methane and benzene with 0.02 % selectivity. Similar selectivities were also obtained on experiments operated on spray-pulse reactor [27].

2.3 Environmental and health impacts

The LOHC technology has great potential to decrease the greenhouse gases emitted by the automotive and transport industry by avoiding the use of gasoline. Some preliminary estimates conclude that a 40 % reduction in CO_2 emissions could be achieved by normal passenger cars by replacing gasoline with LOHC powered fuel cells [7]. However, the environmental and health impacts of LOHC compounds must be assessed and possible risks have to be reported to obtain social acceptance for the technology. In general, chemicals are environmentally safe if they are biodegradable, non-toxic and non-accumulative and will not break-down to harmful products [28].

The burning of hydrogen itself does not produce any emissions, but the LOHC compounds and their decomposition products can possess some environmental and health hazards. LOHCs are neutral organic compounds with poor water solubility and, as such, exposure via water is not likely [28]. With these kind of compounds, most likely exposure routes are via digestion or skin contact. Low water solubility also indicates low toxicity but does not exclude it. For extremely hydrophobic compounds such as perhydro-dibenzyltoluene, chronic effects cannot be ruled out by acute toxicity tests [28]. These compounds should thus be investigated more closely for chronic effects. Furthermore, the compounds might be accumulative in living organisms.

As mentioned earlier, benzyltoluene and dibenzyltoluene are environmentally hazardous and may cause long lasting harmful effects to aquatic life. They may also be fatal if swallowed or if the compound enters airways [15], [16]. However, they are biodegradable and do not exhibit significant bioaccumulation. As the substances show chronic toxicity in aquatic life, chronic effects on humans are also possible.

N-ethylcarbazole has no toxicological information available. It is classified as irritant substance, which causes skin irritation, serious eye irritation and may cause respiratory irritation [29]. It has also been found to exhibit no biodegradability during a 4-week experiment in diluted microbial community. In addition, partially hydrogenated NEC, H8-NEC, can be classified as potentially bio-accumulative due to its $K_{o/w}$ value being higher than 4.5. It is also classified as potentially toxic by Quantitative Structure-Activity Relationship (QSAR) tests [28].

Methylcyclohexane and its dehydrogenated form toluene are classified as flammable and irritant. They also possess health hazards. Furthermore, methylcyclohexane is classified as environmentally hazardous. Both compounds are highly flammable and cause skin irritation. They may cause drowsiness or dizziness and might be fatal if swallowed or if the compound enters airways. MCH is also very toxic to aquatic life, causing long lasting effects whereas toluene is suspected to cause damage to unborn children and organs through prolonged or repeated exposure. Neither of the compounds are considered to be bio-accumulative. Toluene is readily biodegradable whereas methylcyclohexane is not biodegradable. [30], [31]

The main decomposition products of BT/DBT decomposition are methane, toluene, benzene, methylcyclohexane and cyclohexane [4]. Methane and benzene are also obtained from MCH decomposition [26] whereas carbazole and methane are formed in NEC decomposition [19]. The health and environmental hazards of methylcyclohexane and toluene were assessed in the previous paragraph. Cyclohexane has the same environmental and health hazard classifications and warnings as methylcyclohexane, with the distinction that it is slightly less toxic to aquatic life and it is biodegradable [32].

Methane is formed by decomposition from all presented LOHC compounds as all of them have a methyl group attached to them. Methane is an extremely flammable gas. In addition, methane might be harmful or irritant if inhaled or if let in contact with the skin or eyes [33]. Furthermore, methane is over 25 times more potent greenhouse gas than CO_2 as it's more efficient in trapping radiation [34]. However, its lifetime in the atmosphere is significantly shorter compared to CO_2.

Benzene is classified as flammable, carcinogenic and irritant. It may cause cancer, genetic defects and damage to organs through prolonged or repeated exposure. Furthermore, benzene causes irritation to skin and eyes and it is even possibly fatal if swallowed. In addition, it is harmful to aquatic life with long lasting effects. Because of its many hazardous qualities, extensive protective equipment must be used when handling benzene. Benzene is not classified as bio-accumulative and it is readily biodegradable. [35]

Carbazole is classified as carcinogenic and it is suspected of causing cancer and long lasting harmful effects to aquatic life. It is slightly bio-accumulative. There is no data available whether carbazole is biodegradable or not. [36]

Even though the conversion of LOHC compounds to decomposition products is small (0.02 % for MCH, 0.2 % for DBT/BT and max. 1 % for NEC [2]), because the used LOHC is recycled, the degree of decomposition and the amount of harmful decomposition products might reach significant levels through repeated usage. Because of this, the severe health and environmental risks posed by some of the decomposition products must be taken in to consideration when designing LOHC technology equipment. One advantage that LOHC system has over fossil fuels is that the components in LOHCs are known whereas the composition of e.g. crude oil can vary depending on the oil's origin [28]. This makes the assessment and management of the risks much easier.

3. Catalysts for dehydrogenation

3.1 General

Efficient catalysts are required for the dehydrogenation of LOHCs. The main properties for dehydrogenation catalysts are excellent selectivity towards dehydrogenation products, good stability and low amount of deactivation by e.g. coking [7]. The catalytic dehydrogenation includes the adsorption of the LOHC compound on the catalyst's surface followed by rapid abstraction of the hydrogen atom and formation of a pi-bond. In order to avoid reverse reaction on the catalyst's surface, rapid removal of the hydrogen atom and formation of molecular hydrogen is essential [7].

3.2 Noble metal catalysts

Typically, noble metal catalysts have been used for dehydrogenation of LOHCs [2], [26], [37]. Especially platinum catalysts are well studied by many different groups [27], [38]–[41], but also palladium catalysts have been used in some studies [42].

For BT and DBT, platinum-based catalysts have been found to be superior. The most common supports for platinum catalysts have been alumina and carbon, with carbon yielding better degree of dehydrogenation and higher total volume of H_2 released. [2]. In different experiments, the amount of Pt loading has varied between 0.5 wt-% and 5 wt-% [2], [4], [43].

N-ethylcarbazole dehydrogenation has been typically catalyzed with either platinum or palladium on alumina support [2], [22], [42]. For example, for their batch reactor experiment, Brückner et al. [2] used Pd/Al_2O_3 catalysts with 0.5 wt-% loading, whereas Peters et al. [22] used commercial platinum catalyst powder with 5 % Pt on alumina.

For the dehydrogenation of MCH, platinum catalysts are used with alumina being the most common support material [26], [37], [44]. However, Shukla et al. [6]

conducted an extensive study on the effects of the support material to the hydrogen evolution rate in the dehydrogenation of MCH. They found that lanthanum oxide La_2O_3 has significantly higher hydrogen conversion rate than e.g. alumina or titania. Yet, the Pt/La_2O_3 catalyst showed poor selectivity towards the dehydrogenation reaction. However, this drawback was countered by using perovskite $La_{0.7}Y_{0.3}NiO_3$ as a support instead of La_2O_3 as this perovskite was found to be highly selective towards the dehydrogenation reaction. The amount of Pt loading on support varied between 0.6 wt-% and 3 wt-% [6], [26], [37].

In the case of BT/DBT and MCH, reducing the amount of metal loading has been found to result in better H_2 release when compared to higher percentage loading with identical overall amount of metal [2], [6]. For example, decreasing the amount of Pt loading in DBT dehydrogenation from 5 wt-% to 1 wt-%, the degree of dehydrogenation increased from 55 % to 71 % [2]. The higher degree of dehydrogenation on lower metal loading degrees is expected to be caused by higher dispersion of the active metal, which increases the selectivity towards the dehydrogenation reaction [6].

3.3 Bimetallic catalysts

In order to reduce the amount of noble metal and the cost of the catalyst, bimetallic catalysts can be used. One promising option is to use nickel-based catalyst with small amount of noble metal. In an experiment carried out by Biniwale et al. [41], catalyst with 20 wt-% Ni and 0.5 wt-% Pt on activated carbon support was used in cyclohexane dehydrogenation. This Ni-Pt catalyst exhibited over 60 times higher hydrogen production rate compared to 0.5 wt-% Pt catalyst, with 99.7 % selectivity to hydrogen. Similar findings were made by Kariya et al [27]. In their experiments, Pt-Rh catalysts showed higher activities compared to monometallic Pt catalyst in cyclohexane dehydrogenation. This was thought to be caused by the combination of the electronic effect of Rh to Pt and the synergistic effect of rhodium's C-H bond cleavage ability and platinum's high hydrogen recombination ability. In addition, bimetallic platinum catalyst with Ir and Re have shown to have higher activities compared to monometallic Pt catalysts in cyclohexane dehydrogenation [45]. No studies have been conducted on the effect of bimetallic catalysts in the

dehydrogenation of other LOHC compounds, but as the positive effects seem to be based on the added metals and not on the dehydrogenated compounds, they might be applicable to other LOHCs as well.

3.4 Catalyst deactivation

Kreuder et al. [37] have shown some Pt/Al_2O_3 catalysts to deactivate rapidly in MCH dehydrogenation, losing most of their activity after three hours of use, due to coke formation at ambient temperature and normal dehydrogenation temperature of 350 °C. The deactivation time can be influenced with temperature, (modified) residence time and pressure. In the experiments of Kreuder et al. [37], the modified residence time was defined as the ratio of catalyst mass to volume flow of MCH (kgs/m^3). Higher temperature resulted in a higher coke formation rate and thus higher deactivation rate. At 420 °C, the relative deactivation was 50 % after 200 min whereas the relative deactivation was only 20 % after 200 min at 325 °C, with the same modified residence time [37]. Higher modified residence times, i.e. lower volume flow of MCH, resulted in lower deactivation rate and higher initial conversion as the compound was in contact with the catalyst longer and the load on the catalyst was smaller due to lower feed rate. For example, at 325 °C with the modified residence time of 4000 kgs/m^3, the initial conversion of MCH was almost 100 % and the relative deactivation after 200 min was approximately 20 %. With modified residence time of 2000 kgs/m^3 at the same temperature, the initial conversion was 70 % and the catalyst lost its activity almost completely after 100 minutes [37]. Finally, higher pressures (9 bar compared to 1 bar) were utilized to inhibit the deactivation. At higher pressures the initial conversion was lower (60 % compared to 100 %), but the rate of deactivation was low as the level of conversion was stable for 800 min at 9 bar where as it would gradually decrease to zero at 1 bar during an 800 min experiment run [37].

Co-feed or internal recirculation of hydrogen also decreases the deactivation rate [26], [37]. In the catalyst life time experiments by Okada et al. [26], the catalyst showed only minor deactivation during 6000 h period when a co-feed of hydrogen was used. The initial co-feed of hydrogen was 20 mol-% and it was decreased down to 5 mol-% during the experiment. Thus, they concluded that 5 % co-feed of

hydrogen is sufficient for pure methylcyclohexane feed to inhibit catalyst deactivation.

Kreuder et al. [37] also found that the deactivated catalyst can be regenerated by oxidizing the catalyst in air at high temperatures (400 °C). However, the number of regeneration cycles affects the activity of the catalyst. After 16 regeneration cycles, the catalyst has 20 % higher relative deactivation after 200 min compared to a fresh catalyst.

Sebastián et al. [46] have studied Pt/C catalyst activity with another viable LOHC compound: decalin. During the experiments, some deactivation was observed. The deactivation may be the consequence of adsorption of the dehydrogenated compound naphthalene on the catalyst surface. Naphthalene has high boiling point and affinity for the active carbon, thus requiring high energy to be removed from the catalyst surface. It is unknown, whether similar deactivation is possible with benzyltoluene or dibenzyltoluene.

For palladium catalysts, no deactivation studies have been carried out with the LOHC compounds discussed in this thesis, but some experiments have been executed with other dehydrogenation reactions. Similar to Pt/Al_2O_3 catalysts, Pd/Al_2O_3 catalysts show deactivation by coke formation in dehydrogenation of n-butane [47]. In the dehydrogenation of a LOHC type compound, tetrahydrocarbazole, Pd/Al_2O_3 catalyst showed deactivation also by poisoning i.e. the strong adsorption of an unwanted compound on the catalyst surface [48]. However, it was possible to counter this effect by washing the catalyst with a base, in this case NaOH, prior the use [48].

4. Reactor concepts for LOHC dehydrogenation

Many different types of reactors have been tested and studied for the release of hydrogen from LOHC compounds ranging from conventional batch and fixed bed reactors to more novel monolithic reactors [49]. Currently, only one commercial LOHC energy production unit exists. This unit is manufactured by the Hydrogenious Technologies GmbH. The unit is presented in Figure 5. It consists of a LOHC storage vessel, 100 kW dehydrogenation unit heated by hydrogen burner and a 30 kW PEM fuel cell. The LOHC compound used in this commercial unit is perhydro-dibenzyltoluene [21].

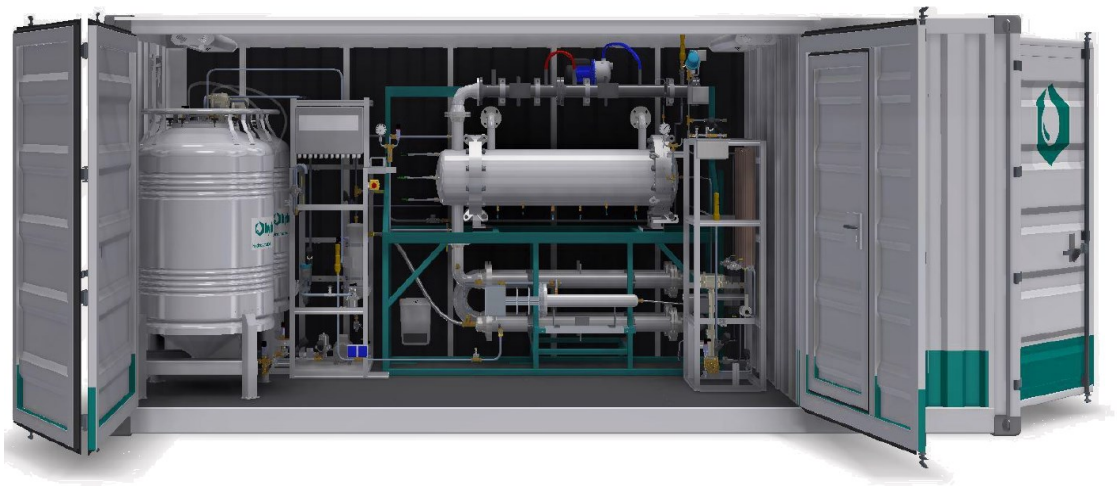

Figure 5. Commercial LOHC demonstration unit by Hydrogenious Technologies GmbH. Consist of LOHC storage vessel (left), dehydrogenation unit (middle) and PEM fuel cell (right). Reproduced from [50].

In this chapter, different reactor concepts suitable for LOHC dehydrogenation are presented and evaluated. Finally, a comparison between the reactor concepts will be presented.

4.1 Fixed bed reactor

Fixed bed reactors are commonly used in the chemical industry, most commonly for gas phase reactions in large scale production of basic chemicals and intermediates. They have also been used in many different hydrogenation and dehydrogenation reactions. In a fixed bed reactor, catalyst particles are

immobilized, and the reactant feed flows through the catalyst bed causing a chemical reaction on the surface of the catalyst particles. The parameters needed for fixed bed reactor design are: dimension and shape of the catalyst, inlet reactant concentration, linear velocity, length of the reactor and catalyst bed (residence time) and inlet temperature. In addition, the heat of reaction, reaction kinetics and internal characteristics of the catalyst must be known [51]. The basic scheme of a fixed bed reactor is presented in Figure 6.

Figure 6. Basic scheme of a fixed bed reactor. Reproduced from [51].

Fixed bed reactors have been used in several LOHC studies, most notable made by Fikrt et al. [4], where they manufactured a complete lab-scale LOHC unit with reactor volume of approximately 0.7 dm^3. In their configuration, they combined a dehydrogenation unit with a gas liquid phase separator, active carbon filter for gas purification and finally a PEM fuel cell for energy production. In their experiment, the dehydrogenation unit was a fixed bed reactor comprising of a horizontal tube, with the length of 2.5 m and diameter of 19 mm, filled with Pt/Al_2O_3 catalyst and heated with heating oil. The LOHC compound used was H18-DBT. They were able to produce constant, continuous release of hydrogen with their setup. Thus, it has been demonstrated, that a fixed bed reactor dehydrogenation unit can be successfully used in a complete LOHC energy production process, albeit external heating is required. In addition to Fikrt et al., also Shen et al. [48] showed that hydrogen can be produced continuously from tetrahydrocarbazole with a fixed bed reactor without catalyst deactivation when LOHC is co-fed to the reactor with propene. The reactor setup of Shen et al. consisted of a fixed trickle bed reactor,

with LOHC recycling, which was heated with a furnace to the reactor temperature of 150 °C.

Typically, three parameters can be changed to modify the hydrogen output of the dehydrogenation unit with a fixed bed reactor, or other similar reactor type e.g. membrane reactor or heat exchanger reactor, and the following fuel cell: temperature in the reactor, LOHC mass flow and pressure in the reactor [4]. Increase in temperature results in faster kinetics and higher reaction rate. Because the dehydrogenation is endothermic, the higher temperature also causes higher driving force for the reaction. Changing the temperature is the slowest method to adjust the rate of hydrogen release because of the generally high thermal inertia of the system [4]. Thus, it takes long time to reach the new set point after the temperature has been changed. This problem can be alleviated by using an efficient heat exchanger or utilizing a heat exchanger reactor, which are discussed in a later section. If the mass flow of LOHC is increased, the degree of dehydrogenation is decreased, due to the residence time being lower, but the hydrogen release rate increases because the reaction rate is faster at lower degrees of dehydrogenation. Changing the flow rate offers a more dynamic adjustment method for the hydrogen release rate as a significant change in the hydrogen output is observed within 10 minutes after changing the flow rate [4]. The amount of hydrogen released can be quickly adjusted by changing pressure. By lowering pressure, the hydrogen release rate can be increased and vice versa due to the le Chatelier's principle. However, this will only change the rate of hydrogen release momentarily, so this method can only be used as a buffer while the chemical reaction rate is adjusted by other parameters to attain the new hydrogen release set point permanently [4].

Fixed bed reactors have also been used in the development of LOHC dehydrogenation catalysts. Okada et al. [26] used platinum catalyst on 1 mm alumina beads in a stainless steel tube reactor with diameter of 12.6 mm. In this reactor, they studied the dehydrogenation of methylcyclohexane and observed that the platinum catalyst is suitable for a continuous constant production of hydrogen. They also used hydrogen co-feed, which allowed the catalyst to remain stable for 6000 h.

Overall, fixed bed reactors seem promising for the dehydrogenation of LOHC compounds, as one fully functional lab-scale energy production unit utilizing LOHC technology in a fixed bed reactor has already been assembled [4]. The general advantages of fixed bed reactors in LOHC dehydrogenation are stable and continuous hydrogen production and relatively simple design. However, there are some reports noting that the reverse hydrogenation reaction of dehydrogenated LOHC compounds might be favored in fixed bed reactors, which might limit the usage of fixed bed reactors or at least affects the optimization of the reactor [49]. This might be due to hydrogen staying in contact with the catalyst after its release and possibly creating higher local hydrogen pressures, favoring the reverse hydrogenation reaction. However, in well-designed reactors the hydrogen flow out of the reactor should be quick enough not to create favorable conditions for the reverse reaction. Furthermore, the catalysts used for the LOHC dehydrogenation are not usually the most favorable for the LOHC hydrogenation, so the reverse reaction should not be probable.

4.2 Membrane reactor

In a membrane reactor, a membrane serves as a product distributor, a reactant distributor or a catalyst support. In the reactor, the reaction mixture and the catalyst are surrounded by a membrane, which is selectively permeable to at least one of the products. For example, a tubular membrane reactor consists of two co-axial tubes, where the inner tube is made of the membrane material. The product of the reaction goes through the membrane to the permeate chamber, where it is usually swept away from the reactor by an easily separable sweep gas. The sweep gas can be fed in to the reactor co-currently or counter-currently with respect to the reacting mixture. In an experiment carried out by Li et al. [52], a co-current stream of nitrogen sweep gas was utilized in hydrogen production by ammonia decomposition. The sweep gas acted as a driving force for the permeation of H_2 gas through the membrane. In their experiment, the usage of nitrogen sweep gas was found to increase the conversion of NH_3 from 45 % to 95 %. However, the separation of the sweep gas from the product gas requires additional equipment, which is unfavorable. In LOHC dehydrogenation applications, where pure hydrogen is produced at atmospheric pressure from pressurized LOHC

compounds, such as methylcyclohexane, it is favorable to feed the hydrogen directly to a hydrogen station or a fuel cell. This method of direct hydrogen feeding was used for example by Akamatsu et al. [53], [54]. In most applications, the catalyst is either packed as a tight bed outside of the inert membrane or allowed to move more freely in a fluidized state in the close vicinity of the membrane. This way, when the catalyst is not inside the membrane, the system is easier to operate, and the separation capability of the membrane can be changed independently of the catalyst's activity. In other applications, catalyst can be coated on the membrane's surface or it can be dispersed inside the membrane's structure. Reactors where the catalyst is dispersed inside the membrane are typically called catalytic membrane reactors (CMR) [55], [56]. Schemes of co-current and counter-current tubular membrane reactors are presented in Figure 7.

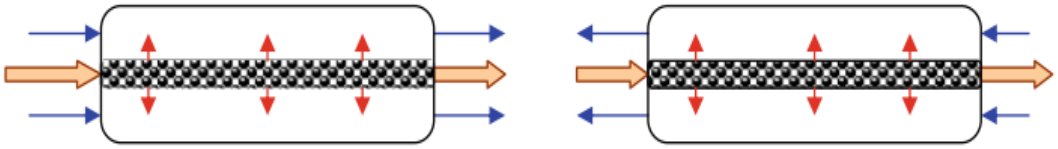

Figure 7. Schemes of co-current and counter-current tubular membrane reactors. Reproduced from [55].

The main advantages of the membrane reactors are combining a chemical reaction with the product separation in a single unit and the ability to increase the conversion beyond the thermodynamic equilibrium. This is achieved by removing products from the reaction mixture and thus prohibiting the reaction to reach the chemical equilibrium. For example, Meng and Tsuru [44] reported that, by removing hydrogen from the reactor in methylcyclohexane dehydrogenation at 250 °C, the conversion almost doubled from the equilibrium value of 44 % to 86 %. Conversely, the same conversion can be obtained at lower temperatures with membrane reactor compared to a fixed bed reactor. Lower operating temperatures in turn allow safer operation and lower operation costs. Lower temperature also decreases the degree of catalyst deactivation by decreasing the amount of sintering and the amount of coke deposition on the catalyst surface [55], [56].

Some technical difficulties have, however, occurred with membrane reactors. If the membrane is damaged, the whole system needs to be shut down to empty the

reactor of the catalyst and reaction mixture, change the membrane and start up the system again. To counter this drawback, Staged Membrane Reactors (SMR) have been proposed [55]. SMRs comprise of a reactor, followed by a membrane separation unit, where one of the products is separated from the mixture. After separation, the reaction mixture is transferred to a second reactor followed by another separation step. In theory, the system can comprise of as many reactor and separation steps as needed. Figure 8 shows a schematic of SMR with two reactors and separation units. However, this type of system loses the main advantage of membrane reactors to combine reactor and separation in to one single unit. It has been observed however, that SMRs enhance the performance of the whole system in terms of separation selectivity and yield [57]. Overall, only a few commercial applications of membrane reactors exist as of yet, due to technical difficulties related to membrane stability, mass transfer limitations and high production costs [55].

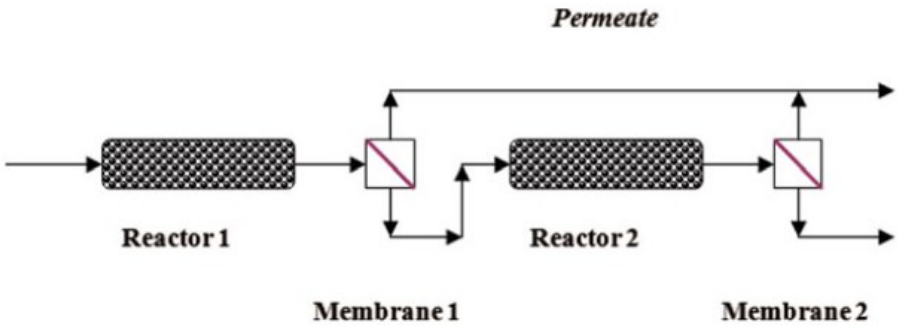

Figure 8. Staged membrane reactor. Reproduced from [55].

The performance of a membrane is evaluated by its permeability, selectivity and stability. Ideally, a membrane would have high selectivity and permeability, but usually maximizing one will decrease the other [56]. From these two characteristics, selectivity is usually prioritized, because low permeability can be compensated to some degree by increasing the surface area of the membrane, whereas low selectivity requires the usage of multi-stage processes [56]. Permeability and selectivity are determined by the membrane's material and structure and they determine the separation mechanism and possible applications of the membrane. For a membrane to be stable in industrial applications, it should have the following properties: chemical resistance, mechanical stability, thermal stability and stable operation [56].

Different membrane materials are suitable for different applications. Inorganic membranes, such as palladium, have high chemical and thermal resistances and mechanical stability. Thus, they are optimal for applications with harsh reaction conditions. The drawback of these membrane materials is their typically high cost [56]. For all reactions involving the generation or consumption of hydrogen, dense palladium or silicate membranes offer good selectivity and permeability. However, pure palladium membranes have some disadvantages, which limit their commercial applicability. For example, pure palladium membranes experience embrittlement when exposed to pure hydrogen at temperatures below 300 °C [55]. They can also be deactivated by carbon compounds at temperatures above 450 °C. Furthermore, the cost of palladium is high. All of these disadvantages can be reduced to some extent by alloying palladium with some other metals, e.g. silver [55]. Silica membranes have also been investigated for dehydrogenation reactions as separation units due to their amorphous structure, which has highly selective permeation towards hydrogen, and lower price compared to palladium membranes [44].

After the reaction mixture has passed through the membrane reactor, it will consist of unreacted raw materials and products, which were not permeated through the membrane. In the case of LOHC dehydrogenation, this mixture would consist of completely dehydrogenated LOHC, partially dehydrogenated LOHC, unreacted LOHC, hydrogen and side products. There is a well applicable solution for treating this mixture in LOHC dehydrogenation. As hydrogen has high energy content, it can be separated from the mixture and burned to generate heat for the reactor while the unreacted compounds would be recycled back to the reactor [55]. Another useful application of this solution could be to recycle the whole remaining reaction mixture back to the reactor as it is. As mentioned earlier, co-feed of hydrogen almost completely eliminates catalyst deactivation in fixed bed reactor experiments [26], so this recycled reaction mixture could act as a catalyst stabilizer. The catalyst is, in essence, deposited as a fixed bed in membrane reactors, so utilizing co-feed of hydrogen to inhibit the catalyst deactivation should be possible also in membrane reactors. No studies have been conducted considering this application, meaning that experiments have to be carried out to determine the composition of the outlet reaction mixture to determine if the amount of hydrogen in the mixture is suitable to be utilized as co-feed. If the hydrogen content is too

high, some of the hydrogen can be separated and fed to a fuel cell or used to produce heat for the reactor, while leaving enough hydrogen (5 mol-% [26]) in the mixture to provide sufficient hydrogen co-feed.

For LOHC dehydrogenation experiments, membrane reactors with palladium and silica membranes have been used [44], [53], [54], [58]. Most of the experiments have been carried out with MCH as the LOHC compound. Itoh et al. [58] used palladium membrane on alumina support with 0.5 wt-% Pt/Al_2O_3 catalyst to study the dehydrogenation of MCH in a membrane reactor. They found that the hydrogen release rate can be increased by decreasing the pressure below atmospheric pressure or by increasing the reaction pressure. This is logical, since the flow of hydrogen through the membrane is driven by the pressure gradient between the two sides of the membrane.

A review article by Meng & Tsuru [44] concludes that catalytic silica membrane reactors offer a feasible and economically attractive alternative to conventional fixed bed reactors and palladium membrane reactors for LOHC dehydrogenation reactions. Especially CMRs with bimodal catalyst support, i.e. support consisting of two different support compounds e.g. α-Al_2O_3 and γ-Al_2O_3, has good potential as it shows significant increase in catalytic activity and stability. Akamatsu et al. [54] have also demonstrated that silica membrane shows good stability during continuous LOHC dehydrogenation for long periods of time. In their experiment, they operated a packed bed silica membrane reactor for 1054 h to dehydrogenate methylcyclohexane. During the experiment, the membrane showed only a small decrease in performance observed as slight decrease in hydrogen purity and conversion. The purity of hydrogen was however, high overall, ranging from 98.5 % to 99.1 %. The same group was later able to develop a silica membrane reactor capable of producing hydrogen with purity up to 99.95 % from methylcyclohexane without using carrier gas or sweep gas [53]. The impurities in the product stream were methylcyclohexane and toluene in these experiments.

In general, membrane reactors offer a great alternative to fixed bed reactors, mainly due to the advantage of obtaining higher conversion than the thermodynamic equilibrium would allow, which is the upper limit for fixed bed reactors. In addition, they offer a simpler operation combining the reaction and

separation of the product in a single operation step. In some cases, membrane reactors can generate hydrogen which is pure enough to be directly fed to a PEM fuel cell without additional purification of the hydrogen. This is possible, when no by-products due to hydrocracking are formed as was the case in the MCH dehydrogenation experiments by Akamatsu et al. [54]. However, the immaturity of the technology and technical difficulties associated with the membranes are challenges that need to be resolved before membrane reactors can be applied to commercial LOHC dehydrogenation concepts.

4.3 Pulse-spray reactor

In a pulse-spray reactor, alternating wet and dry conditions are created on a heated catalyst surface by injecting the reactants on top of the catalyst as an atomized spray i.e. the wet step. Spraying of the reactants occurs in pulses with controlled frequency. After injection, the reactant evaporates on the hot catalyst surface, creating a dense vapor near the catalyst surface. The vaporized reactant can adsorb to the catalyst surface easier, compared to a liquid reactant. Between the two injection pulses, i.e. the dry step, the unreacted reactant and the products are removed from the catalyst surface and transferred out of the reactor. This unsteady state operation improves the stability of the catalyst by keeping the catalyst surface clean, which increases its activity. In the case of LOHC dehydrogenation, where the heat requirement of dehydrogenation is high, the surface of the catalyst can be kept at high temperature to favor the dehydrogenation reaction. A continuous hydrogen production can be achieved with pulse-spray reactors by operating several reactors with a time phase lag. [7] A typical experimental pulse-spray reactor setup is presented in Figure 9.

Currently, no commercial applications for pulse-spray reactors exist, but some development and application tests considering LOHC dehydrogenation have been carried out with them. Biniwale et al. [41], Kariya et al. [27] and Shukla et al. [6], have carried out studies on the pulse-spray reactors to optimize the reaction conditions for cycloalkane, e.g. cyclohexane, methylcyclohexane, decalin and tetralin, dehydrogenation in laboratory conditions. They have also conducted catalyst development experiments for LOHC dehydrogenation reactions on pulse-

spray reactors. Based on the experiments, compared to liquid-solid reaction systems, pulse-spray reactors inhibit the reverse reaction and catalyst site blocking by aromatic by-products such as benzene in LOHC dehydrogenation reactions.

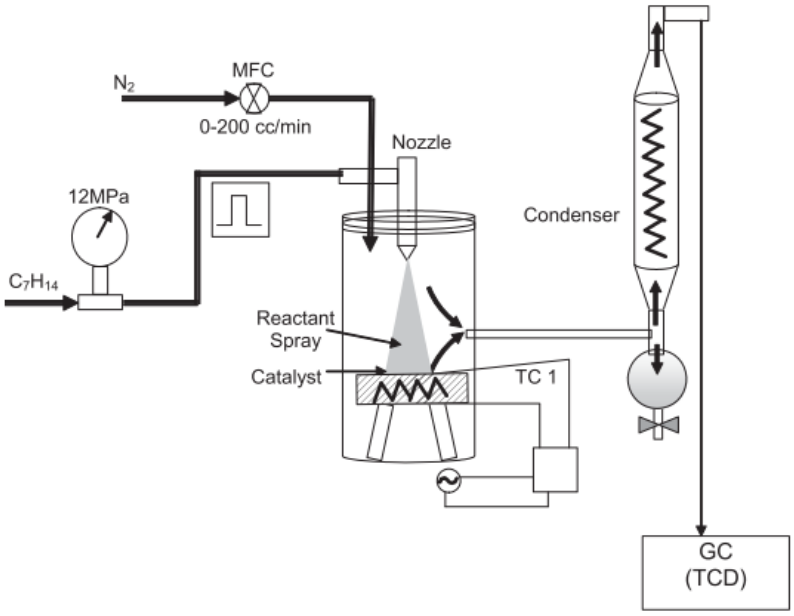

Figure 9. Experimental setup for pulse-spray reactor. Reproduced from [6].

As Shukla et al. [49] conclude in their article, the weaknesses of pulse-spray reactors are their current lack of commercial feasibility and crucial need of intensification. In order to use pulse-spray reactors as continuous and stable hydrogen energy source, several reactors would have to be operated simultaneously. This is problematic due to the space constraints of mobile or portable device applications, which could use hydrogen as energy source. Furthermore, pulse-spray reactors are primarily applicable to LOHC compounds with lower evaporation temperature, e.g. cyclohexane and methylcyclohexane, which do not require as intense heating for evaporation. However, if significant process intensification can be achieved, pulse-spray reactors might be utilized in some LOHC dehydrogenation concepts.

4.4 Thin liquid film state

Reactors utilizing thin liquid films are similar to the pulse-spray reactors. They comprise of heated catalyst bed on top of which the reactant feed is placed as a liquid film either as a batch or the reactant is continuously fed on the catalyst bed. The reactant evaporates from the catalyst surface and exits the reactor to a condenser where it condenses back to liquid and returns to the reactor in batch reactor or exits the system in continuous reactor [59]. As with pulse-spray reactors, this reactor concept is more applicable to LOHC compounds with high vapor pressures as they require less heating in order to evaporate. When the amount of reactant is low and only the catalyst's surface layer is wetted, the system is said to be at liquid film state. Sometimes the catalyst surface layer can become superheated, i.e. its temperature is higher than the boiling point of the solution, when the heating is sufficient. In this "superheated liquid-film state" the conversion of the reactant is increased [59]. Laboratory scale batch and continuous reactor configurations utilizing liquid film state in decalin dehydrogenation are presented in Figure 10.

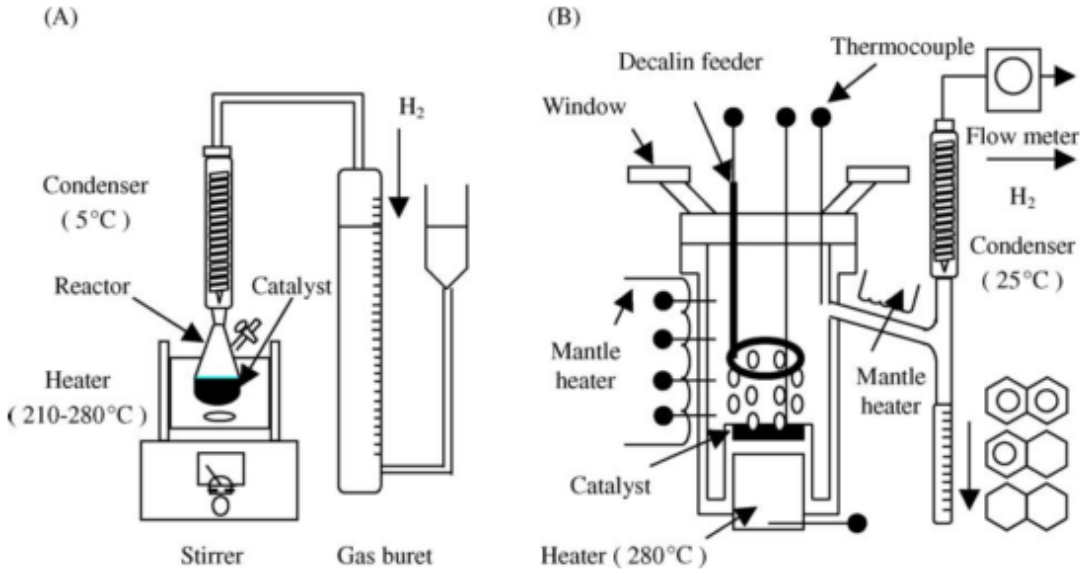

Figure 10. Batch (A) and continuous (B) liquid film state reactor configurations. Reproduced from [59].

Similar to the pulse-spray reactor, reactors utilizing liquid film state do not have commercial applications. Nevertheless, they have been studied for the

dehydrogenation of LOHC compounds. The reactor configuration is mostly developed and most of the research has been carried out by Hodoshima and Saito et al. [39], [40], [59], [60]. They were able to achieve steady and continuous hydrogen release by dehydrogenating decalin in their continuous liquid film state reactor setup, pictured above, at least for the duration of their short (30min) experiments [59]. Other notable achievements of their experiments were high conversions of LOHC compound in short time, up to 95 % in 25 minutes [40] and dehydrogenation past the thermodynamic equilibrium due to the removal of hydrogen from the reactor [39]. They were also able to dehydrogenate methylcyclohexane at as low temperature as 240 °C with high conversion (>90 %) [60]. The conversion they obtained was similar to the one obtained by Okada et al. [26] in their fixed bed experiment performed at 320 °C. Although the lower temperature can, at least partly, be achieved by the usage of different catalyst as Saito et al. used 5 % Pt/C catalyst whereas Okada et al. used 0,6 % Pt/Al_2O_3 catalyst.

Liquid film state reactors suffer from same drawbacks as pulse-spray reactors, granted that only one reactor is needed for continuous hydrogen production. On the other hand, liquid film state reactors do not have the advantages that come with the utilization of wet-dry conditions, such as catalyst cleanliness and stability. As with the pulse-spray reactor, if liquid film reactors can be intensified and commercialized, they could be applied even to mobile hydrogen supply applications.

4.5 Heat exchanger reactor

Heat exchanger reactors have been developed as a form of process intensification. They combine conventional mixing reactors with heat exchangers to enhance the heat transfer capabilities of the reactor. This is achieved by reducing the distance between the chemical reaction site, where the heat is released or needed, and the heat transfer site [61]. Heat exchangers and heat exchanger reactors typically have high specific areas and heat transfer coefficients, so they have better heat and mass transfer properties. Because of this, smaller heat exchanger reactors are needed to obtain the same capacity, compared to e.g. conventional mixing

reactors [61]. The high specific area (small tube diameter) allows the flow to behave similarly to a perfect plug flow in the heat exchanger reactor. This prohibits the formation of dead zones and hot spots in the reactor and increases the selectivity and yield. In addition, the volume of heat exchanger reactors is small, which in turn causes the product quantities to be small. Because of this, operating the reactor is safer, but some capacity issues may emerge [61]. Another advantage of small volume of the reactor is shorter start-up and shutdown periods. The main disadvantage of the heat exchanger reactors are their short residence times ranging from seconds to minutes [61]. As a result, heat and mass transfer must be well optimized to obtain sufficient conversion. However, the short residence times of heat exchanger reactors are not an issue in LOHC dehydrogenation, since the dehydrogenation might not require long reaction times if the heating is sufficient enough, as it should be with a heat exchanger reactor.

One plate type heat exchanger reactor has been patented for possible hydrogen production via LOHC dehydrogenation [62]. Apart from that, only some modelling studies have been conducted on the heat exchanger reactors for LOHC dehydrogenation type reactions [63], [64]. In these studies, a model was constructed for a system comprising of a heat exchange reactor, where an exothermic reaction of methanol synthesis was coupled with an endothermic dehydrogenation of methylcyclohexane. The studies found that using this thermally coupled heat exchanger reactor resulted in smaller reactor size and lower reactor temperature. The heat exchanger reactors can thus offer promising alternative for LOHC dehydrogenation due to good mass and heat transfer properties. Especially micro-structured heat exchanger reactors could be found useful for dehydrogenation processes. However, some drawbacks of heat exchanger reactors have to be solved before they can be used for any industrial applications. For example, catalyst fouling and the resulting deactivation issues still need to be resolved [61]. This problem, however, appears only if the catalyst is coated on the surface of the heat exchanger reactor. If the catalyst is packed between the heat exchanger plates, or inside the pipes, it can be simply changed when deactivation occurs.

4.6 Micro-structured reactor

Similar to the heat exchanger reactors, micro-structured reactors have been developed for process intensification purposes. Micro-structured reactors have attracted attention especially in the energy technology industry, where decentralized and mobile applications are needed [65]. Most of the currently utilized micro-structured reactors are laboratory scale reactors consisting of parallel microchannels with diameters of some millimeters. As mentioned in the previous chapter, these small diameter reaction channels enhance the mass and heat transfer in the reactor.

So far, micro-structured reactors have been used for different type of energy applications, such as reforming of liquid fuels, steam reforming of alcohols and fuel processing. Even complete micro-structured fuel processor prototypes have been manufactured and they have shown good potential in their applications and energy production in small scale. They have also been utilized in Fischer-Tropsch synthesis, methanol and ethanol synthesis and biodiesel production. [65]. A hydrogen storage micro-structured reactor application has also been developed, at least on a model basis [66]. However, in this application the reactor acts as a burner, which heats the hydrogen storage and utilizes the more conventional method of hydrogen burning with oxygen for energy production.

Some LOHC dehydrogenation experiments have been carried out on micro-structured reactors, although so far they have mostly focused on catalyst testing and development [37], [67], [68]. Roumanie et al. [67], used a microchip developed for biomedical applications to perform methylcyclohexane dehydrogenation and study different catalyst deposition techniques. The chip consisted of a coiled 1.5 mm diameter channel, which was packed with 5 µm circular pillars, totaling the reactor's specific wall area to 12 700 m^2/m^3. Kreuder et al. [37], used a micro-structured membrane reactor for their catalyst deactivation studies. They were able to obtain conversion as high as 95 % with their reactor setup. In addition to experimental studies, one catalytic microchannel reactor has been patented by Toseland et al. [69]. In the system presented in the patent, N-ethyl carbazole is pumped in to series of parallel reaction chambers which are filled with catalyst and heated to e.g. 200 °C. Heat is provided in to the reactor by circulating a heat

exchange fluid through the reactor. For example, combustion of gaseous byproducts or using a heat exchange fluid from a fuel cell are mentioned in the patent as possible means of heat input. The reactor channels are followed by a gas liquid separator, which separates the hydrogen gas from the liquid product. The scheme of the reactor is presented in Figure 11.

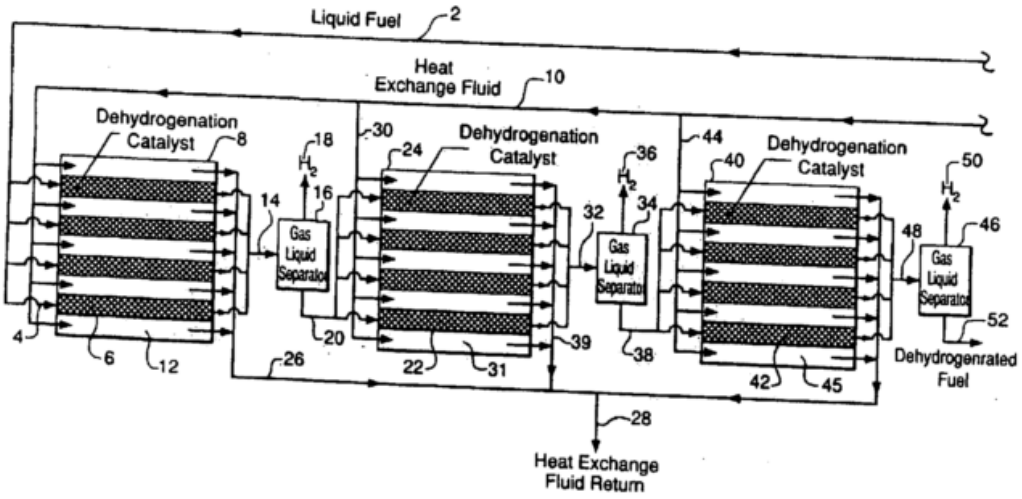

Figure 11. Scheme of catalytic microchannel reactor concept. Reproduced from [69].

Micro-structured reactors have many advantages considering LOHC dehydrogenation concepts. As the reactions are highly endothermic and require excellent phase contact with the catalyst, micro-structured reactors could provide viable solution for these challenges [68]. However, even though micro-structured reactors have a compact design, it is often complex, which results in high capital costs. Furthermore, micro-structured reactors still lack commercial availability, so a great deal of research still needs to be carried out before micro-structured reactors can be fully utilized.

4.7 Monolithic reactor

Monolithic reactors are a type of micro-structured reactors, which consist of a series of narrow parallel channels. Monoliths are characterized by their channel shape, cell density (cells per square inch) and wall thickness. The main advantages of the monolithic reactors are the low pressure drop across the length of the reactor

and high surface area. In the experiments by Liu et al. [70], the pressure drop within the reactor was studied with the dehydrogenation of ethylbenzene in monolithic and packed bed reactors. The pressure drop was found to be approximately 20 times lower in monolithic reactor compared to a conventional fixed bed reactor. The flow in the channels is laminar, which means that narrow (1 μm - 10 μm) channels are needed to ensure that the mass transfer is efficient in liquid phase reactions [71]. The monolithic reactors are usually used at applications, where the low pressure drop within the reactor is essential and efficient heat and mass transfer are needed. They can also be used at applications where significant volume expansion happens, such as endothermic dehydrogenation reactions [22]. However, the good heat transfer capabilities are inherent only in the metallic monolith structures whereas the heat transfer in ceramic monolithic structures is generally low. Monolithic reactors can be constructed either from catalytic material and used as such, or they can be constructed from other materials, e.g. metals or ceramics, on top of which the catalyst is adhered [71]. A typical monolith structure is shown in Figure 12.

Figure 12. Monolith structure in automobile catalytic converter. Reproduced from [72].

One reactor utilizing monolith type structure has been tested for LOHC applications by dehydrogenating H12-NEC [22]. The reactor used, comprised of ten parallel, metallic vertical tubes, with a metallic 3-D structured cellular monolithic network inside the tubes. The diameter of the monolith cells was 4.95 mm and diameter of the pipes were 25 mm. It took 45 minutes for the system to reach steady state, but after this start-up period, the system stayed in a stationary state and showed only small deviations during 48 h experiment. In the experiments, the highest obtained

hydrogen yield was 78.7 % with liquid feed rate of 10 ml/min and the highest hydrogen flow rate was approximately 9.8 l/min with a liquid feed rate of 30 ml/min. With this hydrogen flow rate, an electric power capacity of 960 W could be obtained with a fuel cell with 55 % efficiency. This accounts for a power density of 3.84 kW_{el}/l.

Other type of monolithic reactor considered for LOHC dehydrogenation is based on a monolithic stirrer reactor concept previously reported by Moulijn et al. [71]. However, in the reactor concept considered for LOHC dehydrogenation the monolith structure rotates around a horizontal shaft instead of a vertical one. The monolith structure is coated with the dehydrogenation catalyst and half of the structure is submerged in the liquid LOHC compound. When the monolith rotates, part of the structure wetted with LOHC is lifted above the surface. Thus the structure undergoes alternating wet and dry conditions, which improves the catalyst cleanliness and stability, as reported earlier [73]. The reactor schemes of the monolithic reactor types are presented in Figure 13.

Monolithic reactors, especially the rotating monolithic reactor, present a promising alternative for LOHC dehydrogenation due to their good heat and mass transfer properties, high catalytic surface area, possibility to utilize alternating wet and dry and thin film conditions and low pressure drop across the reactor length [71], [73]. However, the experimental data available for monolithic reactor in LOHC dehydrogenation applications is minimal. Thus, a great deal of research has to be carried out before the monolithic reactors can be applied for LOHC energy production concepts.

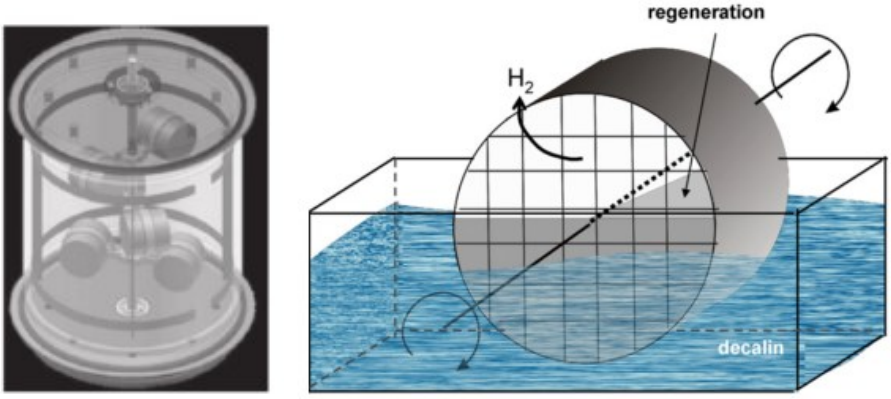

Figure 13. Monolithic stirrer reactor (left) and rotating monolithic reactor concept. Reproduced from [71], [73].

4.8 Comparison of reactor concepts

In this chapter, several different reactor concepts for LOHC dehydrogenation have been presented. The comparison of the attributes of different reactor concepts is presented in Table 2.

Fixed bed reactor is the industrially best established and the most studied of the presented reactor concepts. It is also the only reactor type that has been used for manufacturing a complete LOHC energy production unit, thus far [4]. This proof of concept shows that LOHC technology can already be utilized in commercial applications. However, fixed bed reactor is limited by the thermodynamic equilibrium, high pressure drop and it is also reported to favor the reverse hydrogenation reaction [49].

Some of these drawbacks can be avoided by using either a membrane reactor, heat exchanger reactor, micro-structured reactor or a monolithic reactor. The thermodynamic equilibrium can be surpassed by removing some of the hydrogen from the reactor system by using a membrane reactor. Micro-structured reactors and monolithic reactors can be used for a low pressure drop operation in addition to good mass and heat transfer within the reactor. Similar advantages can be obtained with a micro-structured heat exchanger reactor. It is also possible to combine these properties by attaching a membrane to a micro-structured reactor as was done by Kreuder et al. [37]. However, micro-structured reactors and membrane reactors are more expensive and more difficult to maintain than fixed bed reactors due to their more complicated design.

Utilizing alternating wet and dry conditions by spray pulse system or using superheated thin liquid film conditions have been shown to yield hydrogen with excellent purity and high conversion, while also promoting catalyst stability and activity [5], [60]. However, these technologies suffer from the need of additional equipment such as condensers. Furthermore, to obtain continuous yield of hydrogen from spray pulse systems, several reactors have to be used. These drawbacks make the commercialization of these technologies difficult for mobile applications. They might, however, find use in e.g. backup energy production applications for households.

Alternating wet and dry conditions and their inherent advantages can also be obtained with a rotating monolithic reactor proposed by Lázaro et al. [73]. This reactor concept shows the most potential for LOHC dehydrogenation concepts, at least in theory. It combines the great structural, heat and mass transfer properties of monolithic reactors with the advantages of increased catalyst activity and stability provided by the alternating wet and dry conditions. In addition, this concept should not have size constraint issues as it only consists of a vessel filled with LOHC and a rotating monolith structure, making it applicable to mobile applications as well. However, it remains to be seen if this potential can be realized as no experiments have yet been reported with this type of reactor.

Table 2. Comparison of different reactor concepts.

Reactor type	**Continuous operation**	**Maturity of technology**	**Applicability/ Compactness**	**Mass/ heat transfer**	**Wet and dry conditions**
Fixed bed	+	+++	+	-	-
Membrane	+	++	++	+	-
Pulse-spray	-	-	-	++	+
Thin liquid film	+	-	-	++	-
Heat exchanger	+	+	+++	+++	-
Micro-structured	+	+	+++	+++	-
Monolith	+	-	+++	+++	+/-

In the table, a minus sign denotes a lacking or non-existent property, one plus sign denotes that the property exists but it is limited. Two plusses denote that the quality of the property is good, and three plusses denote an excellent quality.

5. Materials and methods

This chapter describes the experimental work, that was carried out. The experimental setup and working methods are described as well as the calculation and product analysis methods.

5.1 Experimental setup and experimental work

5.1.1 Experimental setup

The experiments were carried out on a laboratory scale setup, of which a schematic is presented in Figure 14.

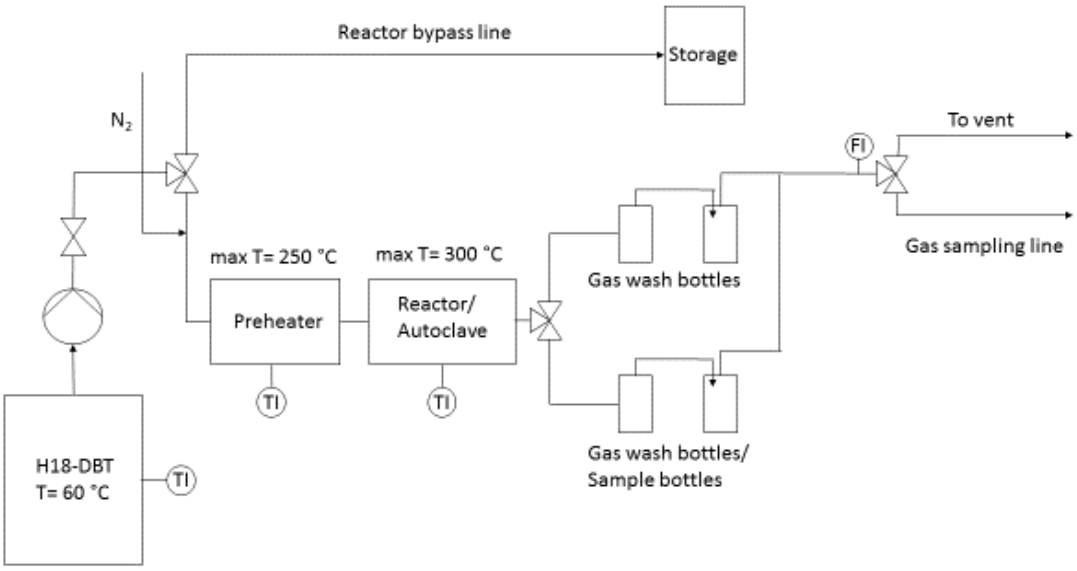

Figure 14. Schematic of the experimental setup.

In the experiments, H18-DBT MARLOHC 18/90 (Sasol), which was 95 % hydrogenated and acquired from Hydrogenius GmbH, was used as the LOHC compound. An ordinary one-liter laboratory glass bottle with a cap was used as a feed tank. The bottle was heated to 60 °C with an electric heating tape, to decrease the viscosity of the H18-DBT, thus making it easier to pump the liquid through the lines. The H18-DBT is pumped from the feed bottle through a polytetrafluoroethylene (PTFE) pipe, which was inserted in to the feed bottle

through a hole in the cap of the bottle. In general, all the pipes in the system were PTFE pipes, excluding those that were directly in contact with either the preheater or the autoclave. These pipes were stainless steel 316 as PTFE might degrade at 300 °C.

The pump used in the experiments was a HP-1050 isocratic HPLC pump, manufactured by Hewlett Packard. The flow rates used in the experiments were between 0.03 ml/min and 0.11 ml/min. It was observed that, for H18-DBT, the highest flow rate that could be obtained with this pump was approximately 0.25 ml/min due to the high viscosity of the fluid. Prior to starting the experiments, the pump was calibrated by setting a pump flow rate, pumping the substrate through the reactor system and measuring the actual flow rate at the outlet. Based on these measurements, a calibration curve was formed.

The preheater comprised of a coiled 119 cm 1/8” diameter stainless steel pipe, around of which a metallic electric heater was wrapped. The inside of the coil was filled with glass wool and a thermometer was placed between the heater and the pipe as shown in Figure 15. Finally, the coil was wrapped in glass wool and aluminum foil to ensure good insulation. During the experiments, the preheater was set to 250 °C.

Figure 15. Preheater used in the experimental work. Photo by Aki Braunschweiler.

The autoclave used in the experiments was a one-liter stainless steel 316 autoclave, which was manufactured by Amar Equipments PVT. Ltd. The design pressure of the autoclave was 100 bar and the design temperature was 300 °C. The autoclave was filled with Therminol® 62 synthetic heat transfer fluid. The autoclave had a built in electric heater, thermometer, pressure meter and a stirrer with water cooling. The stirrer was operated at 116 rpm.

Two types of tube reactors were used in the experiments, depending on the catalyst packing method. Both reactors are shown in Figure 17. For packed bed experiments, a 24 cm U-tube reactor with an inside pipe diameter of 4 mm was used, whereas for the washcoated catalyst experiments a coiled 143 cm tube reactor, with the same inside diameter as U-tube, was used. The reactors were manufactured from Inconel 600 pipe. The U-tube was packed by inserting the catalyst from both ends of the pipe and measuring the length of the empty space on top of the bed to determine the beds length. On the end of the bed, a 1.5 cm layer of quartz wool was densely packed to hold the catalyst in place.

Figure 17. U-tube reactor and coiled washcoated reactor used in experiments. Photo by Aki Braunschweiler

From the reactor, the liquid product and the formed gases were directed to the impinger bottles either in the bypass line or sampling line. The liquid product is trapped in the bottles and the gases flow through the bottles to either vent or gas

sampling bag. In both lines, two bottles in series were used. In the bypass line, the first bottle was filled with isopropanol up to one third of the volume of the bottle. The second bottle was filled with glass beads up to one third of its volume to improve the gas-liquid contact. The volume of the gas washing bottles in the bypass line was approximately one liter. In the sampling line, the bottles were smaller, approximately 0.1 liter. One fourth of the volumes of both bottles were filled with glass beads and in the first bottle, the beads were submerged in isopropanol. In addition, the second bottle was placed in an ice bath. In both lines, the liquid was typically completely trapped in the first bottle.

A Bronkhorst Low ΔP-Flow F-201D 50 ml/min mass flow controller was used to measure the hydrogen outlet flow. Prior to use, the controller was calibrated with nitrogen. The catalyst activity was measured with this mass flow controller. A decrease in the gas flow, i.e. the amount of hydrogen generated, indicated a decreased catalyst activity. The catalyst activity was measured in this way during long experiment runs for different catalysts

5.1.2 Experimental work

All the experiments were carried out in a similar manner. After the reactor setup was assembled, the heating of the reactor was started. The temperature was gradually increased by 25-50 degrees at a time. At this point, also the autoclave's stirrer was started with a stirring speed of 116 rpm. During the heating, the lines were flushed with nitrogen to remove air from the system. When the temperature was approximately 50 degrees from the reaction temperature, the pump was switched on. The pump was first purged with the pump's built-in purge mode to remove possible air bubbles from the lines. After the purge, the filling of the lines was started with the maximum pumping rate (0.25 ml/min) in order to fill the lines as quickly as possible. Before starting the pump, the nitrogen flow was stopped. At this point, the pre-heater was set to 150 °C. The temperature of the heater would typically overshoot to approximately 300 °C after which, the heater was set to its set point value of 250 °C.

After the lines were filled, the pumping rate was set to the flow rate corresponding to the desired liquid hourly space velocity (LHSV) or weight hourly space velocity (WHSV). As the amount of catalyst in particle and washcoat reactor setups was

different, a constant LHSV or WHSV was used for experiments instead of a constant flow rate. Thus, the flow rate relative to the mass or volume of the catalyst would be the same in all the experiments and the results would be more easily comparable. The LHSV was used in the experiments where the catalyst was in a particle form as a packed bed whereas WHSV was used in the washcoat experiments. The flow rates used in the experiments and their corresponding space velocities are presented in Table 3. After setting the flow rate, the system was left to reach the steady state. At this point, the fluid flow was directed to the bypass lines. The approach to steady state was monitored with the gas flow meter. When the meter's percentage value stabilized, i.e. the gas flow remained constant, the system was determined to have reached steady state. The system typically reached the steady state in an hour. At this point the fluid flow direction was changed from the bypass line to the liquid sampling line. The system was left to stabilize again as the product gases flush out possible air left in the liquid sampling impinger bottles. After approximately 20 minutes, the gas sampling bag was opened, and the gas flow was directed to the gas bag. After the gas bag was filled with enough gas for analysis and enough liquid was gathered in the sampling bottle, the gas bag was closed, and the fluid flow was directed back to the bypass line. The liquid sample intake would typically last approximately from one to two and a half hours, depending on the volume flow. The gas sampling typically took between 20 and 45 minutes. If several experiments were to be carried out on the same day, the flow rate and temperature were changed to the next set point value and the system would be left to attain the new steady state. Otherwise, the pump was switched off and the temperatures of the autoclave and pre-heater were decreased to 200 °C and 80 °C, respectively. Finally, the lines were flushed thoroughly with nitrogen overnight to remove any liquid still in the lines.

Table 3. Summary of set-point flow rates corresponding to different space velocities for different catalysts.

LHSV (h^{-1})	**1**	**2**	**3**
WHSV (h^{-1})	**1.51**	**3.05**	**4.57**
Catalyst	**Flow rate of H18-DBT (ml/min)**		
Pt/Al_2O_3 particle	0.031	0.061	0.092
Pt/Al_2O_3 washcoat	0.036	0.072	0.107
Pt/C particle	0.030	0.061	0.091
Pt/TiO_2 washcoat	0.015	0.030	0.046

The liquid sample impinger bottles were detached from the system and the liquid left in the line was flushed in to the bottle with 10 ml of isopropanol. The inlet and outlet lines were then detached from the bottles and the bottles were emptied to a 250 ml Duran capped laboratory glass bottle. Because some of the liquid sample might have been transported from the first bottle to the other as aerosols by the product gases, the bottles and the couplings between the bottles were flushed in to the 250 ml glass bottle with isopropanol. The bottle with only glass beads in it, was flushed three times and the bottle with glass beads and isopropanol was flushed five times. The 250 ml bottle was then capped, labeled and stored at a refrigerated room. The product gas bag was labeled and stored at ambient temperature and pressure.

5.2 Catalysts

5.2.1 Catalysts used in the experiments

Platinum catalysts were used in all the experiments. Three different support materials were tested in total, to observe differences in hydrogen production with different catalyst supports. The used supports were alumina, titania and activated carbon. Of these three, alumina was used as a packed bed and washcoat whereas

titania was only used as a washcoat and activated carbon was only used as a packed bed. All the catalysts were designed and prepared at VTT and University of Helsinki. The catalysts were prepared by impregnation. The diameter of the catalyst particles in the packed bed was 0.2-0.3 mm and the targeted active metal loading was 1 %. The amounts of catalyst used in the experiments are presented in Table 4.

Table 4. The amounts of catalyst used in the experiments

Catalyst	Packing	Weight (g)	Volume (ml)	Bed length (cm)
Pt/Al_2O_3	packed bed	1.108	1.834	14.6
Pt/Al_2O_3	washcoat	1.298	-	-
Pt/C	packed bed	0.959	1.822	14.5
Pt/TiO_2	washcoat	0.55	-	-

5.2.2 Catalyst characterization

The Pt/Al_2O_3 catalysts were characterized using hydrogen chemisorption to obtain information about the dispersion of the active metal. The other catalysts were not analyzed with chemisorption due to time constraints. The chemisorption measurements were carried out at Aalto University School of Chemical Engineering by the Department of Chemical and Metallurgical Engineering's Catalysis research group. The equipment used was a Thermo Scientific Surfer Gas Adsorption Porosimeter. The catalyst samples were reduced at 300 °C for two hours and degassed at 300 °C for two hours prior the chemisorption measurement. The chemisorption was carried out at 25 °C under hydrogen gas.

5.3 Analysis of products

5.3.1 Analysis of liquid products

The liquid products were analyzed with an Agilent Technologies 6890N gas chromatograph. The chromatograph was equipped with an Agilent 7683B Series injector, Agilent 5973 Network Mass Selective Detector and an Agilent Ultra 2 column (50 m x 0.32 mm ID, 0.52 µm film). Helium was used as a carrier gas. The

initial temperature of the column was 70 °C. The oven program was 70 °C – 2 min – 20 °C/min – 160 °C – 2.5 °C/min – 320 °C, which amounts to total run time of 70.5 min. In the analysis, solvent delay of 2 min was used, so the large amount of isopropanol in the sample would not be detected. An example of a GC-MS chromatogram is presented in Appendix 2.

A NMR measurement was carried out for some samples to obtain accurate information about the degree of dehydrogenation of the sample and to verify the accuracy of different calculation methods. The NMR analysis was carried out on Varian 300 Hz NMR-spectrometer. Prior to the sample analysis, isopropanol was evaporated from the sample. Methylenechloride-d2 was used as a solvent in the NMR samples. The NMR measurements were carried out at the University of Helsinki.

5.3.2 Analysis of gaseous products

The gas samples were analyzed for decomposition products using an Agilent Technologies 7890B gas chromatograph with PD-HID detector. The amounts of carbon monoxide, carbon dioxide and methane were analyzed from the gas samples. The gas chromatograph was calibrated using a 10 ppm CO, 10 ppm CO_2, 10 ppm CH_4 calibration gas in helium. The column used in the gas sample analysis was an Agilent HP-5 column (30 m x 0.32 mm ID, 0.25 µm film). The initial temperature was 40 °C and an oven program of 40 °C – 20 °C/min – 120°C – 1 min was used. The total run time was 9 min.

5.4 Calculation methods

5.4.1 Space velocities

The liquid hourly space velocity (LHSV) can be calculated with Equation 1,

$$LHSV\left(\frac{1}{h}\right) = \frac{\dot{V}_{in}}{V_{cat}}, \quad (1)$$

where

$\dot{V}_{in}$ liquid flow in to the reactor (ml/h), and

V_{cat} volume of the catalyst in the reactor (ml),

and weight hourly space velocity (WHSV) can be calculated with Equation 2

$$WHSV\left(\frac{1}{h}\right) = \frac{\dot{m}_{in}}{m_{cat}}, \quad (2)$$

where

m_{in} mass flow in to the reactor (g/h), and

m_{cat} mass of the catalyst (g).

LHSV can be changed to WHSV by calculating the volume flow of certain LHSV, converting the volume flow to mass flow and calculating the WHSV of this flow. This is shown in Equations 3 and 4, WHSV is again calculated with Equation 2.

$$\dot{V}_{in} = LHSV \cdot V_{cat}, \quad (3)$$

$$\dot{m}_{in} = \dot{V}_{in} \cdot \rho, \quad (4)$$

where

ρ density (g/cm^3).

The space velocities were predetermined for the experiments and the required flow rate for each space velocity was calculated with the two aforementioned equations. The flow rate was converted to the pump's flow rate setting using the pump/flow calibration curve.

5.4.2 Degree of dehydrogenation

The degree of dehydrogenation (dodh) was calculated based on the volume flow of hydrogen out of the reactor, measured by the mass flow controller, and the raw material flow in to the reactor. From the raw material flow, the amount of hydrogen bound to the LOHC flowing in to the reactor, i.e. the theoretical maximum of released hydrogen, F_{in,H_2}, can be calculated with Equation 5,

$$F_{in,H_2}\left(\frac{ml}{min}\right) = F_{in,tot}\left(\frac{ml}{min}\right) \cdot x_{H18-DBT} \cdot w_{H_2}, \quad (5)$$

where

$F_{i,tot}$	total raw material flow in to the reactor (ml/min),
$x_{H18-DBT}$	amount of LOHC in the raw material (purity), and
w_{H_2}	hydrogen weight capacity for the LOHC compound.

The volume flow out of the reactor was calculated from the mass flow controller reading with the calibration curve with Equation 6,

$$\dot{V}_{H_2}\left(\frac{ml}{min}\right) = [k \cdot V(\%) + b] \cdot 1000\, ml/l, \qquad (6)$$

where

$V(\%)$	percentage value reading of the flow controller,
k	slope of the calibration curve, and
b	intercept of the calibration curve

The calibration curve for the 50 ml/min hydrogen mass flow controller is shown in Figure 16.

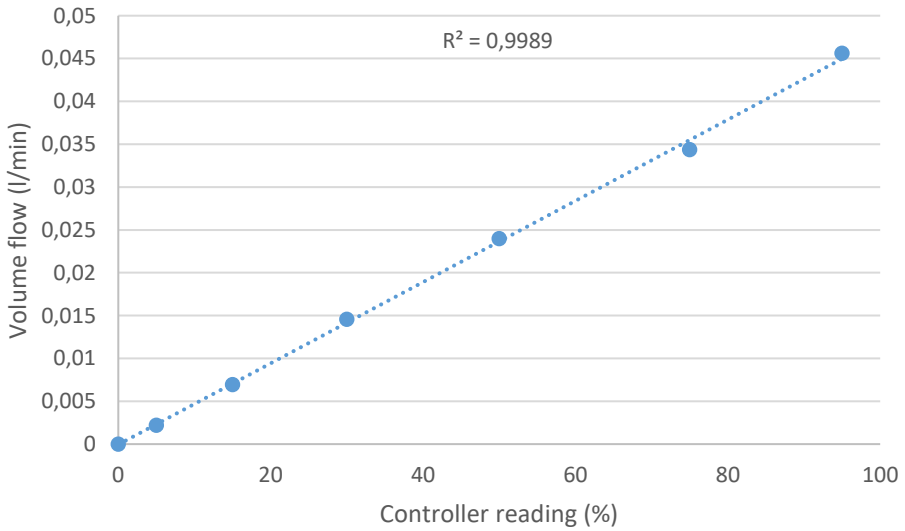

Figure 16. Calibration curve for the 50 ml/min hydrogen mass flow controller.

From the volume flow, the molar flow of hydrogen can be calculated with the ideal gas law, Equation 7,

$$\dot{n}_{H_2} = \frac{p\dot{V}_{H_2}}{RT}, \quad (7)$$

where

$\dot{n}_{H_2}$	molar flow of hydrogen (mol/min),
p	ambient pressure (Pa),
$\dot{V}_{H_2}$	volume flow of hydrogen (ml/min),
R	ideal gas constant, 8314000 $\frac{cm^3 \cdot Pa}{K \cdot mol}$, and
T	ambient temperature (K).

In the experimental setup, the mass flow meter is separated from the reactor with series of lines, meaning that the hydrogen is approximately at room temperature when it enters the flow meter. In the calculations, an approximate of the average room temperature (23 °C) was used, as there were no means of collecting accurate temperature data during the experiments.

The mass flow of hydrogen can be calculated from the molar flow with Equation 8,

$$\dot{m}_{H_2} = \dot{n}_{H_2} \cdot M, \quad (8)$$

where

M	molecular weight of the compound (g/mol).

Finally, the degree of dehydrogenation (dodh) can be calculated from the mass flow of hydrogen out of the reactor and the theoretical maximum hydrogen flow (hydrogen content of the inflow) with Equation 9,

$$\mathrm{dodh} = \frac{\dot{m}_{H_2}}{F_{i,H_2}}. \quad (9)$$

The degree of dehydrogenation was also calculated based on a method proposed by Modisha et al. [74]. In this method, the degree of dehydrogenation was calculated based on the gas chromatography mass spectrometry (GC-MS) analysis. The peaks of LOHC compounds with different degrees of dehydrogenation (H0, H6, H12, H18-DBT) are separated based on their mass

spectra (m/z values). Their m/z values are 272, 278, 284 and 290, respectively. The degree of hydrogenation (doh) of the liquid sample is then calculated from the mole fractions of the different compounds, which are obtained from the mass spectra peaks, using the Equation 10 [74],

$$\text{doh} = 0.33(X_{H6-DBT}) + 0.67(X_{H12-DBT}) + X_{H18-DBT}, \quad (10)$$

where

X_i mole fraction of compound i, (Total peak area of compound i) / (Total peak area of all compounds).

The degree of dehydrogenation is then calculated from the degree of hydrogenation with Equation 11,

$$\text{dodh} = 1 - \text{doh}. \quad (11)$$

5.4.3 Product decomposition

The product's degree of decomposition (dodc) is calculated based on GC-MS mass spectra by dividing the area of the mass spectrum peaks of decomposition products with the area of all product peaks as shown in Equation 12,

$$\text{dodc} = \frac{A_{dec}}{A_{total}}, \quad (12)$$

where

A_{dec} sum of the areas of decomposition mass spectra peaks, and

A_{total} sum of the area of all product peaks (main products + decomposition products).

The relative amounts of different decomposition products x_i in the mixture can be calculated similarly with Equation 13,

$$x_i = \frac{A_i}{A_{dec}}, \quad (13)$$

where

A_i area of the compound *i*'s mass spectra peak.

This method should yield trustworthy results as no peak overlapping occurs when peaks are separated by their mass spectra and comparison between peaks areas can be performed more clearly. However, some error is inherent in the results due to the number of different isomers in the product mixture.

The reactant H18-DBT mixture contained some decomposition products, approximately 0.18 %, which need to be taken in to account when calculating the degree of decomposition. The reactants decomposition analysis is presented in Appendix 3 together with its mass spectra. Equation 14 can be used to calculate the total degree of decomposition.

$$\mathrm{dodc}_{\mathrm{total}} = \mathrm{dodc}_{product} - \mathrm{dodc}_{reactant}, \quad (14)$$

where

$\mathrm{dodc}_{product}$ degree of decomposition of the product, and

$\mathrm{dodc}_{reactant}$ degree of decomposition of the reactant.

6. Results

Three different types of experiments were executed: experiments with different LHSV or WHSV to test the effect of change in flow rate on the release of hydrogen, the effect of temperature on the catalyst activity and the decomposition of the LOHC compound and longer experiments to test the activity and stability of the catalyst during continuous operation.

All the different types of experiments were carried out on Pt/Al_2O_3 particle and washcoat catalyst systems to observe the differences in hydrogen production on these individual setups. Temperature and catalysts activity experiments were also carried out on the Pt/TiO_2 washcoat system to compare the different catalyst supports. The experiments carried out on different catalysts is presented in Table 5. The (x) denotes that the experiments were carried out only partially. A list of all experiments is presented in Appendix 1.

Table 5. Experiments carried out on different catalysts.

Experiment	**Pt/Al_2O_3 particle**	**Pt/Al_2O_3 washcoat**	**Pt/C particle**	**Pt/TiO_2 washcoat**
LHSV/WHSV	x	x	(x)	
Temperature	x	x		x
Catalyst activity	x	x		x

6.1 Catalyst characterization

The results of Pt/Al_2O_3 catalysts hydrogen chemisorption measurements are presented in Table 6. The dispersion of the active metal was similar in both of the Pt/Al_2O_3 catalysts used in the experiments.

Table 6. Chemisorption results for Pt/Al_2O_3 catalysts

	Pt/Al_2O_3 packed bed	**Pt/Al_2O_3 washcoat**
Amount of H_2 chemisorbed ($\mu mol/g_{cat}$)	8.4	7.4
Metal surface area, sample (m^2/g_{cat})	0.45	0.40
Metal surface area, metal (m^2/g_{cat})	46.0	39.5
Dispersion	16 %	14 %
Mean particle diameter, sphere (nm)	6.2	7.1

6.2 Release rate of hydrogen

Three different space velocities were used for both catalyst systems in the experiments: LHSVs of 1, 2 and 3 h^{-1}, which correspond to WHSVs of 1.52, 3.05 and 4.57 h^{-1}. The LHSV/WHSV experiments were carried out at 300 °C. In the results, the LHSVs used in the packed bed experiments are converted to WHSVs to make the comparison of results between the two catalyst systems easier. The release rate of hydrogen as a function of WHSV for Pt/Al_2O_3 washcoat and particle catalysts is presented in Figure 17. The release rate of hydrogen was calculated for all experiments with Equation 6. The release rate of hydrogen was standardized between the packed bed and washcoat experiments by dividing the hydrogen flow rate with the reactant flow rate. Thus, the unit of measurement becomes ($ml_{H2}/ml_{reactant}$ · min). As can be seen from the Figure 17, the packed bed catalyst yields slightly higher release rates of hydrogen at all space velocities than the washcoat catalyst.

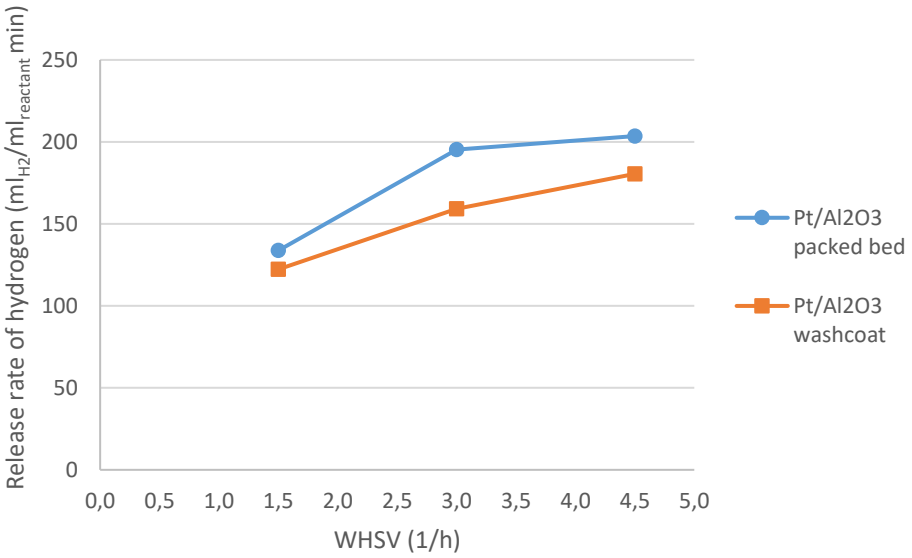

Figure 17. Release rate of hydrogen as a function of WHSV for Pt/Al_2O_3 catalysts at 300 °C.

For all catalysts, excluding Pt/C, four different temperatures were tested: 270, 280, 290 and 300 °C. This temperature interval was based on the heating constraint of the autoclave (305 °C) and the already low flow rate of hydrogen at 270 °C, rendering the experiments on lower temperatures meaningless. The temperature experiments were carried out with LHSV of 3 h^{-1} or the corresponding WHSV of 4.57 h^{-1}. The release rate of hydrogen as a function of temperature for all the catalysts is presented in Figure 18. In can be noted, based on the figure, that the change in temperature causes similar effects for all catalysts and that the titania supported platinum catalyst is the most active catalyst, i.e. it yields the highest release rate of hydrogen.

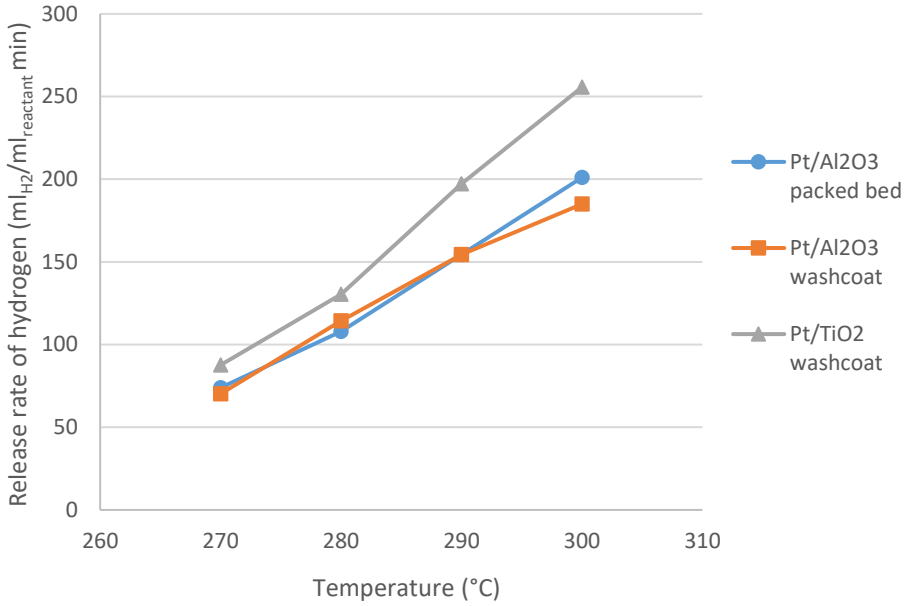

Figure 18. Release rate of hydrogen as a function of temperature for Pt/Al_2O_3 particle and washcoat catalyst and Pt/TiO_2 catalyst with WHSV of 4.57 h^{-1}.

Platinum on activated carbon was also tested at 300 °C and LHSV of 3 h^{-1}. However, the catalyst gradually deactivated almost completely in approximately an hour, and thus, the experiments were not continued.

The replicability of the experiments was tested by carrying out an experiment at the temperature point of 300 °C with WHSV of 4.57 h^{-1} three times for the Pt/Al_2O_3 catalysts and twice for the Pt/TiO_2 catalyst, to observe possible change in the hydrogen production rate caused by catalyst deactivation during the experiments. These experiments were the first space velocity experiment and first and last temperature experiments. It was observed that, for all catalysts, the first experiment would yield different results compared to the other experiments due to catalyst deactivation. Thus, for Pt/Al_2O_3 catalysts, the average of the results from the two latter experiments and the results from the second Pt/TiO_2 experiment were used in the result figures. The deviation of the results is presented in detail in the error estimation chapter.

6.3 Degree of dehydrogenation

The degree of dehydrogenation was calculated based on the hydrogen flow measurement, Equation 9, and GC-MS analysis, Equation 11. The accuracy of these methods was verified with NMR analysis. The GC-MS spectrum shows first the peaks of H18-DBT and after that, the peaks of H12-DBT, H6-DBT and H0-DBT. However, H12-DBT peaks would start to show up in the spectra before all the H18-DBT peaks were detected causing overlapping of the peaks. Similar phenomenon was observed with the peaks of other products as well. This causes the results to be warped because the H18-DBT peaks and H0-DBT peaks would be detected more completely as there are no other peaks at the start and end of the products spectrum. The H12 and H6 peaks on the other hand would overlap with each other and with H18 and H0 peaks. An example of GC-MS spectra is shown in Appendix 2. Peak separation by mass spectra should, in theory, also yield acceptable results as the m/z value should be the same even for different isomers possibly mixed in the mixture and thus the peak areas for different compounds could be calculated. However, this method yielded consistently higher, 5–15 percentage points, degree of dehydrogenation values than the calculations based on the mass flow controller. The calculations based on the hydrogen flow measurement were verified to be the more accurate ones by NMR analysis. Thus, the hydrogen flow rate was used for the calculation of the degree of dehydrogenation. The NMR spectra of H0-DBT, reactant H18-DBT and the spectrum of a product from one Pt/Al_2O_3 packed bed experiment can be seen in Appendix 4.

The degree of dehydrogenation was calculated from the hydrogen flow measured by the mass flow meter and the substrate flow in to the reactor with equations 3-7. The degree of dehydrogenation is presented as a function of WHSV in Figure 19 for alumina support catalysts and as a function of temperature in Figure 20 for all catalysts. As can be seen from the figures, the degree of dehydrogenation is similar for the Pt/Al_2O_3 catalysts and Pt/TiO_2 yields higher degree of dehydrogenation than the alumina supported platinum catalysts.

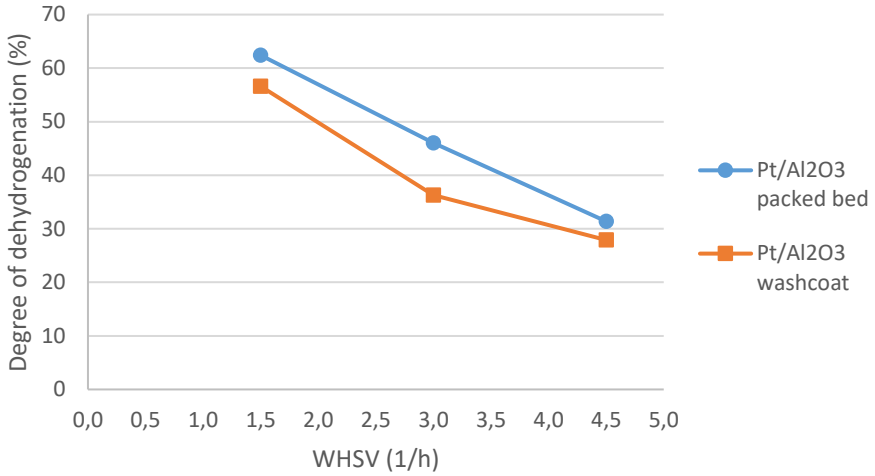

Figure 19. Degree of dehydrogenation as a function of WHSV for Pt/Al_2O_3 catalysts at 300 °C.

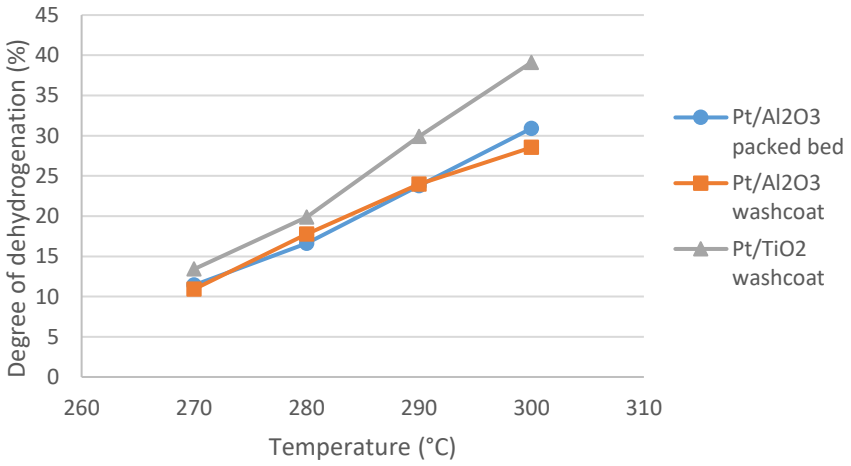

Figure 20. Degree of dehydrogenation as a function of temperature for Pt/Al_2O_3 particle and washcoat catalyst and Pt/TiO_2 catalyst with WHSV of 4.57 h^{-1}.

6.4 Decomposition of H18-DBT

The liquid decomposition products were analyzed with GC-MS. The products observed in the samples were one ring compounds: benzene (m/z=78), methylcyclohexane (m/z=83), toluene (m/z=91); two ring compounds of different degrees of dehydrogenation: H12-benzyltoluene (m/z=194), H6-benzyltoluene (m/z=188) and H0-benzyltoluene (m/z=182) and two ring compounds with an additional methyl group attached to them: methyl-H12-benzyltoluene (m/z=208),

methyl-H6-benzyltoluene (m/z=202), methyl-H0-benzyltoluene (m/z=196). An example of mass spectra of different m/z values can be seen in Appendix 3.

The degree of decomposition of the product samples was calculated with Equations 10 and 12. The results are presented in Figure 21 as a function of WHSV and in Figure 22 as a function of temperature. Figures 21 and 22 show that the degree of decomposition is typically higher in the packed bed catalyst, compared to the washcoat catalysts.

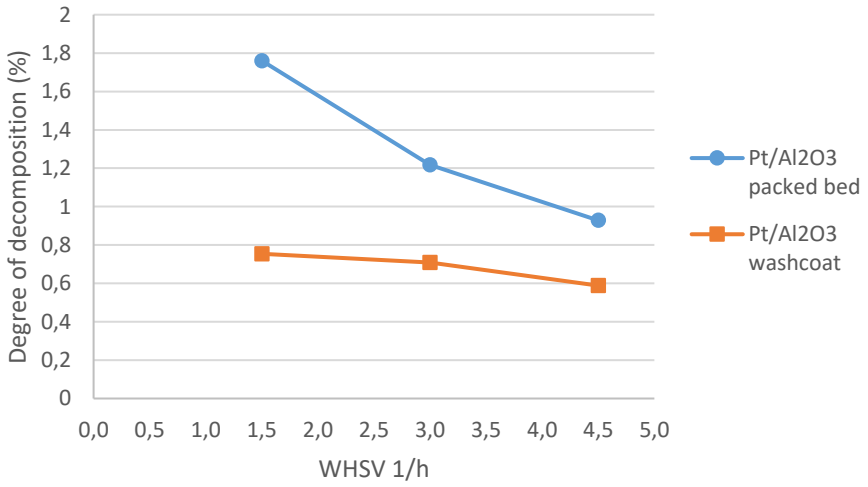

Figure 21. Degree of decomposition as a function of WHSV for Pt/Al_2O_3 catalysts at 300 °C.

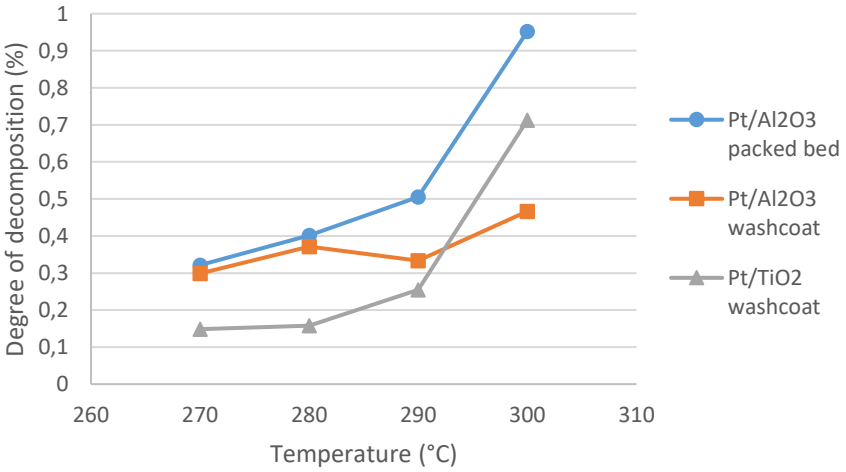

Figure 22 Degree of decomposition as a function of temperature for Pt/Al_2O_3 particle and washcoat catalyst and Pt/TiO_2 catalyst with WHSV of 4.57 h^{-1}.

Finally, the degree of decomposition is presented as a function of degree of dehydrogenation in Figure 23. The data points are from the experiments where the temperature of the reactor was varied between 270 and 300 °C (first point is 270 °C) and WHSV was kept constant at 4.57 h^{-1}. Figure 23 shows the general behavior for all catalysts, which is that the degree of decomposition is proportional to the degree of dehydrogenation.

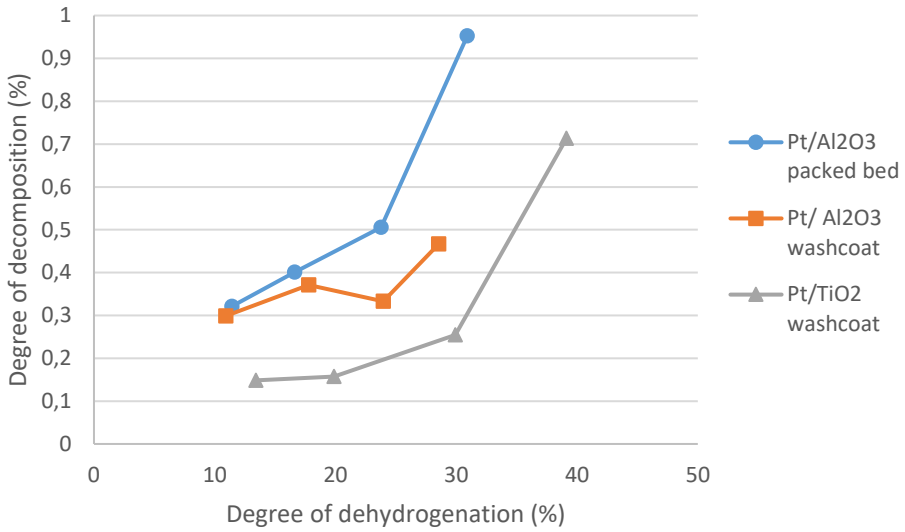

Figure 23. Degree of decomposition as a function of degree of dehydrogenation for different platinum catalysts.

The gas samples were analyzed for methane, carbon monoxide and carbon dioxide. Even though the Pt/C catalyst deactivated rapidly, a gas sample was collected from the experiment and when analyzed, it was found to contain carbon monoxide, making the Pt/C catalyst the only one of the studied catalysts to produce carbon monoxide. In addition, the amount of carbon dioxide did not seem correlate at all with any of the parameters. Thus, only the amount of methane yielded usable results. The amount of methane is presented as a function of WHSV and temperature in Figure 24 and Figure 25.

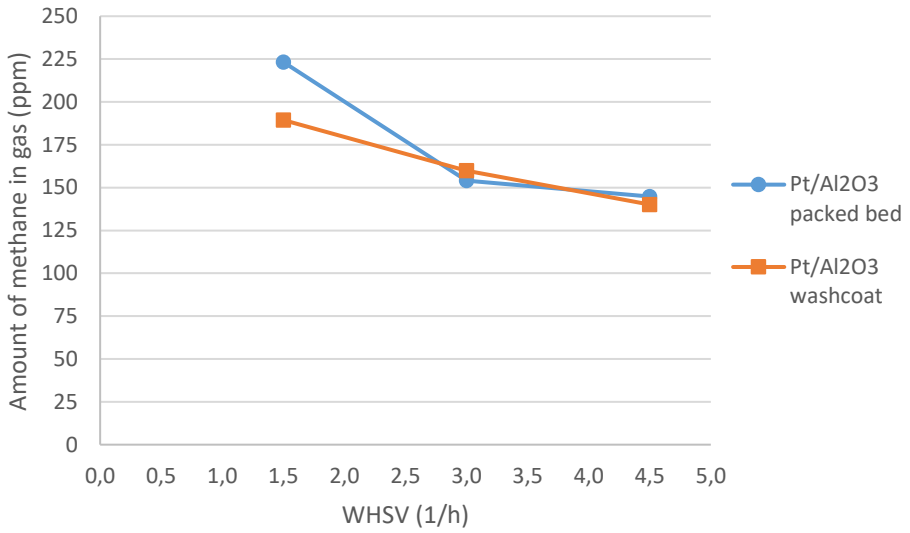

Figure 24. Amount of methane in the product gas as a function of WHSV for Pt/Al_2O_3 catalysts.

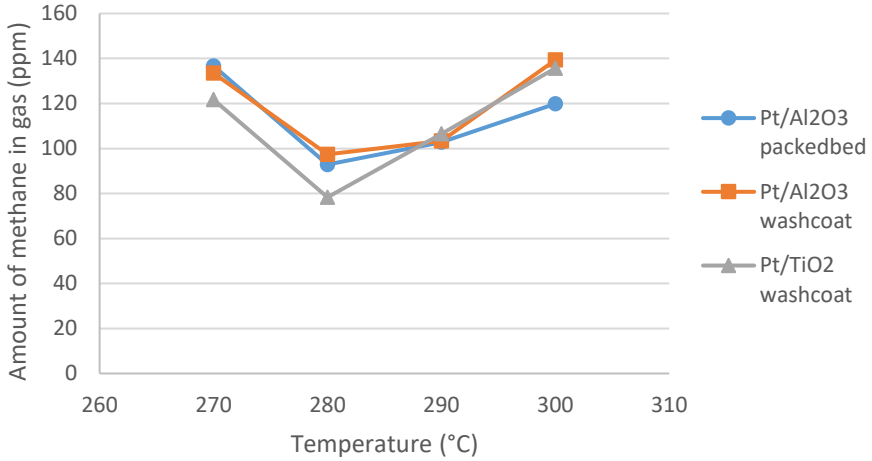

Figure 25. Amount of methane in the product gas as a function of temperature for Pt/Al_2O_3 and Pt/TiO_2 catalysts.

From the figures 24 and 25 it can be seen that the amount on methane in the product gas mixture is similar for all of the studied catalysts at different conditions. The amount of methane decreases similarly for both Pt/Al_2O_3 catalysts as a function of WHSV (Figure 24), which is logical because the degree of dehydrogenation as well as the degree of decomposition decreases as a function of WHSV. An interesting result is that the amount of methane is higher at 270 °C compared to 280 and 290 °C (Figure 25) even though the degree of decomposition is higher at 280 and 290 °C.

6.6 Catalyst long-term activity

After the other experiments, the longer catalyst activity experiment was executed. The long-term activity experiments were carried out at 300 °C and with LHSV of 3 $h^{-}1$ or the corresponding WHSV of 4.57 h^{-1} for 48 h. The change in the catalyst's activity was observed by manually reading the mass flow controller reading. Unfortunately, no computers were available to measure and save the controller data automatically, meaning that the catalyst's activity could only be measured during working hours.

The catalyst activities of different catalysts over 48 h experiment are presented in Figure 26. The experiments were carried out at 300 °C and WHSV of 4.57 h^{-1}. The release rate of hydrogen was standardized for the different catalysts in the same way as was done for the Figure 17 and Figure 18. i.e. the hydrogen flow rate was divided by the reactant flow rate. All the catalyst lost some of their activity over time, but the Pt/Al_2O_3 packed bed catalyst seemed to gain an activity boost after 40 hours of continuous operation. For the other catalysts the deactivation was linear, excluding the rapid deactivation at the start of the experiments. On average, the hydrogen volume flow decreased by 9.0 $ml_{H2}/ml_{reactant}$ min in 10 h for Pt/Al_2O_3 washcoat and 21.4 $ml_{H2}/ml_{reactant}$ min in 10 h for Pt/TiO_2.

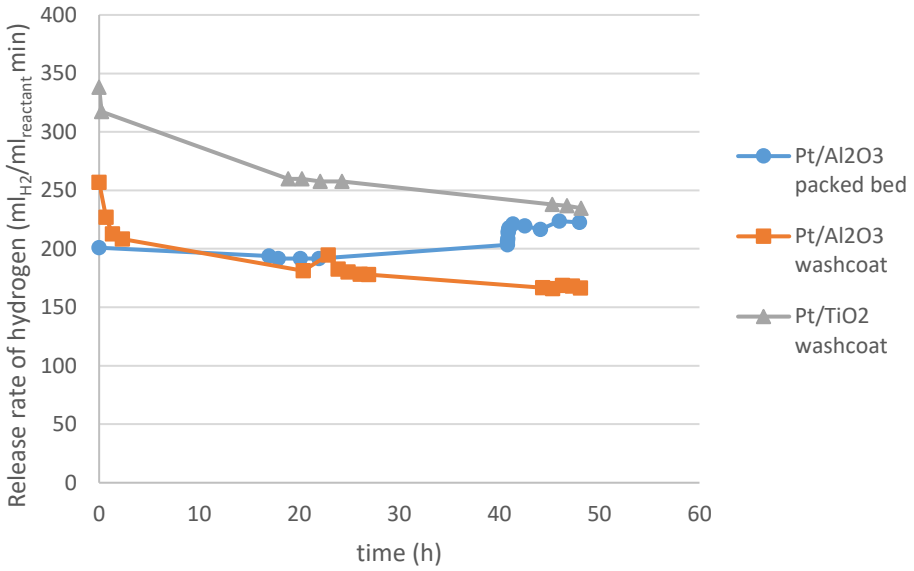

Figure 26. Catalyst activities of different platinum catalysts during 48 h experiment at 300 °C and WHSV of 4.57 h^{-1}.

7. Discussion

7.1 Comparison of different supports

The differences between the used support materials can be observed by comparing the results of Pt/Al_2O_3 and Pt/TiO_2 washcoat catalyst experiments, where the amount of active metal is the same with different supports. From Figure 20 it can be seen that Pt supported on TiO_2 yields overall better degree of dehydrogenation than Pt/Al_2O_3. Similar finding was made by Shukla et al. [6], who also found the Pt/TiO_2 to be slightly superior to the Pt/Al_2O_3.

From Figure 23 it can be seen that the degree of decomposition is also lower on the TiO_2 supported catalyst. At 30 % degree of dehydrogenation, the degree of decomposition is 0.25 % on Pt/TiO_2 catalyst and 0.46 % on Pt/Al_2O_3. Interesting phenomena is observed when the degree of dehydrogenation increases beyond 30 % on the Pt/TiO_2 catalyst as the degree of decomposition increases rapidly. This rapid increase in the degree of dehydrogenation might be a general phenomenon, that when the conversion exceeds a certain level, the degree of decomposition starts to rapidly increase.

As mentioned earlier, a platinum catalyst with activated carbon support was also tested. However, the Pt/C catalyst deactivated rapidly, so no usable results could be obtained. This is unexpected, as the Pt/C catalyst has been found to be the most active catalyst for H18-DBT dehydrogenation [2]. Unfortunately, no reason can be given for the rapid deactivation of the catalyst. Most likely the manufacturing of the catalyst has somehow failed. The reactor system might also have been unsuitable, causing the catalyst to deactivate rapidly. Tentatively, as the Pt/C catalyst produced carbon monoxide, which is toxic to PEM fuel cells, catalysts with activated carbon supports seem unsuitable for commercial applications utilizing PEM fuel cells. However, the formation of carbon monoxide should be verified with an active Pt/C catalyst.

All the other catalysts yielded similar gas composition results with one another. Interesting observation from Figure 25 is that all the catalysts produce the least methane at 280 °C. As the overall degree of decomposition increases as a function

of temperature, it can be said, that the methane cleavage is more favored at 270 °C and 300 °C and at 280 °C and 290 °C the formation of one and two-ringed decomposition products with methyl groups is favored.

Both Pt/Al_2O_3 and Pt/TiO_2 catalysts linearly lost some of their activity during the 48-hour experiment. Interesting anomaly is the increase in Pt/Al_2O_3 packed bed catalyst activity during the 48-hour experiment. Longer experiments with the catalyst should be carried out to determine, if this is in fact a property of the catalyst or just a momentary increase in activity.

7.2 Comparison between the washcoat and packed bed catalysts

A comparison between the washcoat and packed bed catalyst systems can be made by observing the results of Pt/Al_2O_3 packed bed and washcoat catalyst experiments. The catalysts are the same, meaning that the only difference between the catalyst systems is the method of catalyst application, allowing the comparison of the methods.

In general, the different Pt/Al_2O_3 catalysts performed similarly. Both yielded comparable release rates of hydrogen at different conditions and both catalyst systems respond similarly to the change in temperature, as can be seen from Figure 17 and Figure 18. This is expected as the catalysts have the same amount of active metal and similar dispersion (16 % vs 14 %, Table 6). Furthermore, the differences between the reactor systems are structural, or to be more specific, the amount of reactant/catalyst contact is different. As temperature mainly affects the reaction kinetics, which are the same in both reactor systems as the conditions and the catalyst are the same, the responses to change in reactor temperature are similar.

Similar notion can be made about the degree of dehydrogenation, i.e. the conversion of the reactant. The degree of dehydrogenation is slightly higher in the packed bed reactor, but it changes similarly as a function of WHSV and temperature in both reactor systems as can be seen from Figure 19 and Figure 20. With higher space velocities, the residence time is shorter and consequently, the

degree of dehydrogenation is lower. Because the reaction is endothermic, higher temperatures are favorable and increase in temperature increases the degree of dehydrogenation. These responses to change in residence time and temperature are universal and not affected by the method of catalyst placement. The degrees of dehydrogenation obtained for the packed bed catalyst are also well comparable to the results of Fikrt et al. [4]. They obtained a degree of dehydrogenation of 40 % at 300 °C with LHSV of 2.5 (corresponds to WHSV of approximately 3.75). Figure 19 shows that a WHSV of 3.75 would yield a degree of dehydrogenation of approximately 38 % in our packed bed system. In their studies Fikrt et al. used a commercial 0.5 % Pt/Al_2O_3 catalyst as a packed bed.

Even though a higher degree of dehydrogenation is generally favorable, it also causes the degree of decomposition to increase. For both systems the degree of decomposition is proportional to the degree of dehydrogenation as can be seen from Figure 23. However, as the degree of dehydrogenation increases, the increase in the degree of decomposition is much higher in the packed bed reactor. At low conversion levels (10 %), the degree of decomposition is equally low, 0.3 %, for both systems. However, at around 30 % conversion, the degree of decomposition is 0.95 % in the packed bed and only 0.46 % in the washcoat reactor. The same can be observed from Figure 21 and Figure 22. At the lowest space velocity and highest temperature, i.e. the highest level of degree of dehydrogenation, the degree of decomposition in the packed bed reactor is approximately twice as high as in the washcoat reactor. The degrees of decomposition for both systems differ substantially when comparing to the studies of Brückner et al. [2]. In their experiments, the amount of decomposition products on Pt/Al_2O_3 catalyst at 270 °C was less than 0.01 %, where as it was 0.3 % in the experiments carried out for this thesis. Brückner et al. also likely used the same raw material, as it was also manufactured by Hydrogenious Technologies GmbH. The difference in the degree of decomposition might be due to the usage of different reactor systems as Brückner et al. utilized a batch reactor system. In addition, small differences in the catalyst might contribute to the amount of decomposition products as Brückner et al. used commercial catalyst with Pt loading of 0.5 %. The decomposition products obtained by Brückner et al. were methane, toluene, benzene and methylcyclohexane, which are the same as the decomposition products obtained in the experiments for this thesis.

To conclude, the highest degree of dehydrogenation and release rate of hydrogen were obtained at T = 300 °C and WHSV = 1.51 h^{-1}. In the packed bed reactor, the degree of dehydrogenation and release rate of hydrogen were 9.3 % and 18 % higher, respectively, compared to the washcoat reactor. However, at the highest degree of dehydrogenation level, the amount of decomposition products formed in the packed bed reactor was approximately twice the amount of decomposition products formed in the washcoat reactor and the degree of decomposition can be as high as 1.8 %.

7.3 Comparison of reactor concepts for scale-up experiments and commercial applications

Typically, when reactors are scaled up from laboratory scale to, for example, pilot scale, some variable is held constant and other variables are scaled up in relation to this variable. Usually, the variable that is held constant is space velocity or residence time. The space velocity, that yielded the best result in the laboratory scale is chosen and the scale up is then carried out by increasing the fluid flow through the reactor to achieve the desired capacity and increasing the amount of catalyst correspondingly to keep the space velocity constant.

Even though the different catalyst systems performed similarly in the lab scale, differences are to be expected when the setup is scaled up. For example, when flow rates are increased, the packed bed type reactor should show higher increase in hydrogen output compared to the washcoat type reactor. This can be explained by fluid dynamics and catalyst diffusion limitations. As the viscosity of the fluid is high and the inside diameter of the reactor is typically narrow, the fluid flow inside the reactor is laminar. In laminar flow, mass transfer in the radial direction occurs only through diffusion. For the reaction to take place, the reactant has to get in contact with the active metal on the catalyst surface. Outside the catalyst surface is a stagnant film, through which the reactant has to diffuse in order to get in contact with the catalyst surface. This film causes the external diffusion limitation of catalyst particles [75]. The thickness of this film is dependent on the flow rate around the particle. With higher flow rates the film is thinner and diffusion limitations are smaller and vice versa. Thus, at higher flow rates the apparent reaction rate and

consequently, the release rate of hydrogen are higher, if the external diffusion limits the reaction rate. Due to the laminar flow profile, the reactant is in contact with the catalyst only at the reactor walls in washcoat catalyst reactor system. On the other hand, when the catalyst is as a packed bed, the reactant is in contact with the catalyst across the whole reactor. Thus, as the flow rate is increased, the positive effect on the release rate of hydrogen is amplified in packed bed reactors where the reactant is in better contact with the catalyst compared to washcoat reactors. Because H18-DBT has high viscosity, achieving turbulent flow, and the more efficient mass transfer caused by it, might prove to be difficult even in larger scale. Thus, compared to washcoat reactors, packed bed reactors should yield higher degree of dehydrogenation and hydrogen release rate in larger scale experiments.

Another variable, when comparing lab scale experiments to a larger scale, is the heat transfer. In lab scale, where the diameter of the reactor is small, and the heat transfer is efficient, the temperature should be uniform across the whole diameter of the reactor. When the diameter of the reactor is increased, the temperature may vary between the reactor wall and the center of the reactor if the heat transfer is not efficient. Especially, when the fluid flow inside the reactor is laminar. The endothermic reaction inhibits the heat transfer further, as a portion of the heat is always used by the reaction. In the packed bed reactor, the heat transfer should be slightly better compared to the washcoat reactor as the catalyst bed will cause the fluid to mix, at least to some degree, when it flows through the bed. However, other problems arise when packed bed reactors are scaled up. The length of the bed cannot be increased indefinitely, which means that the diameter of the bed (reactor tube) has to be increased as well. This leads to the temperature gradient problems mentioned earlier. Furthermore, when the size of the catalyst bed is increased, at some point also the size of the catalyst particles must be increased as well to avoid the pressure difference across the catalyst bed from rising excessively. The increase in the particle size of the catalyst in turn affects the mass transfer negatively. In addition, even though the heat transfer is better in packed bed reactors compared to washcoat reactors, the heat transfer is still low in packed beds without efficient external heating or the utilization of a heat exchanger reactor.

In the washcoat reactor, scaling up inhibits both, the mass, and heat transfer, at least if the scale up is performed by increasing the reactor tube diameter. However,

generally a better method to scale up washcoat reactors is to increase the number of reactor tubes as increasing the diameter of the tube does not increase the catalyst surface area substantially. Another method is to use washcoated catalyst on a different type of reactor e.g. plate heat exchanger reactor.

The packed bed reactor is expected to outperform the washcoat reactor in the larger scale, at least to some degree. However, in the packed bed reactor, the degree of decomposition is much higher compared to the washcoat reactor, even more so, when the degree of dehydrogenation increases. Thus, even though the packed bed performs better and is overall quite promising concept for LOHC dehydrogenation, as was discussed in the literature part, washcoat reactors should be generally preferred over packed bed reactors in commercial applications. In commercial applications the amount of harmful decomposition product, such as benzene, must be minimized and the recyclability of the LOHC compound should be maximized. These properties are easier to achieve with a washcoat reactor. The heat and mass transfer problems of washcoat reactors can be solved for the most part with reactor design. As mentioned in the literature part of the thesis, heat exchange reactors and micro-structured reactors offer enhanced mass and heat transfer properties. The reactor used in the experiments was a small-scale heat exchanger reactor, where the reactor tube was heated with external heating oil. As was demonstrated by the results of the experiments, at small scale the performance of packed bed and washcoat catalysts is equal and the degree of decomposition is approximately twice as low in the washcoat reactor. Thus, one possibility for larger scale washcoat reactor is to simply increase the number of reactor tubes. In this multitubular heat exchanger reactor, the tube diameter would be narrow and thus, the heat and mass transfer would remain efficient. The optimal tube diameter would have to be determined with future experiments. Another possibility is to design a different type of micro-structured or monolith reactor with optimized heat and mass transfer properties.

One problem however remains with the washcoat reactors. When the catalyst deactivates in the washcoat reactor, the whole reactor tube has to be changed as the catalyst coating cannot be removed once adhered to the reactor wall. This makes the maintenance and applicability of the washcoat reactors more difficult, compared to packed bed reactors where the catalyst can be simply replaced, when

it deactivates. Thus, if washcoat reactors are to be used in commercial applications, the catalyst needs to retain its activity for long periods of time and the reactors should be designed in such a way, that the changing of the reactor tubes is simple. When designed in this way, the time required for the maintenance of the reactors would be minimal and the applicability of the reactor concept is as good as possible. If micro-structured or monolith reactors are used, this process becomes simpler, as the whole reactor could possibly be changed at once, whereas with multitubular reactor one might need to change the tubes one by one. This, of course, can be determined by intelligent reactor design.

8. Error estimation

8.1 Experimental work

During the experimental work, several sources of error could be identified. As there were no temperature measurement units in the room where the experiments were carried out, there is error in the hydrogen flow rates caused by the fluctuation of the room temperatures. In this case, the error is approximately 1 %. This error margin is depicted in Table 7 with different possible temperatures. In the calculations a temperature of 23 °C was used.

Table 7. Error caused by the fluctuation of the room temperature

T (°C)	V (ml/min)	deviation
25	26.81	0.68 %
23	26.63	0
20	26.36	1.01 %
18	26.18	1.69 %

The flow rate has the second largest error. The pump used in the experiments was calibrated before the experiments, but the calibration curve did not fit perfectly to the data points. The pump's calibration curve is presented in Figure 27.

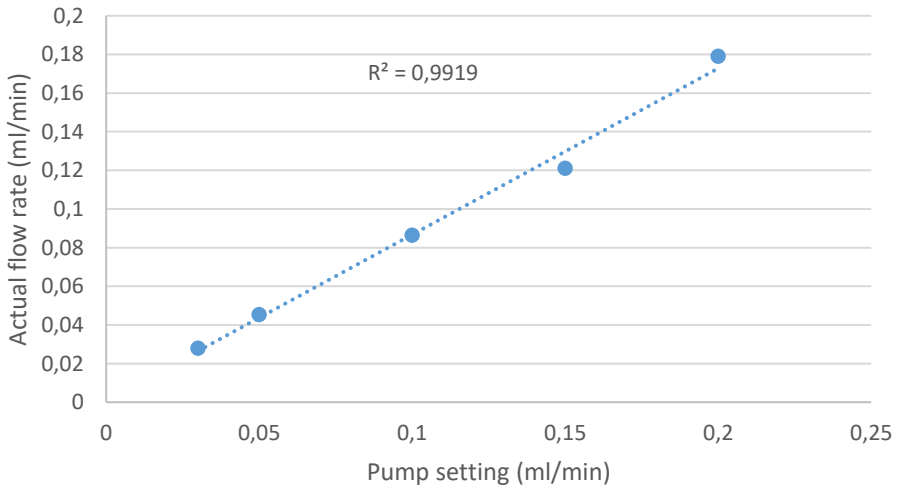

Figure 27. Calibration curve of the isocratic HPLC pump.

As can be seen from the figure, the calibration fits with 99.2 % accuracy, meaning that, on average, there is approximately 0.8 % error in the flow rate, which affects the results slightly. In addition to the liquid flow rate, a small error is expected to be inherent in the gas flow rate as well. As can be seen from the hydrogen mass flow controller calibration presented in Figure 16, the calibration curve fits with 99.9 % accuracy, so the error in the gas flow rate can be expected to be approximately 0.1 %. In addition, as the pump's flow rate's accuracy was only three decimals, the actual flow rate would differ slightly from the desired flow rate.

Another source of error is the stability of the reactor temperature. The temperature of the heater and therefore the temperature of the heating oil would fluctuate slightly causing an instability in the reactor temperature. However, this fluctuation was typically only 0.1-0.2 °C. The maximum error caused by temperature fluctuation is then 0.07 % (0.2 °C error at 270 °C). Thus, the effect on the results caused by temperature fluctuation is insignificant.

In the catalyst activity experiments, some amount of error is caused by the method of measuring the catalyst activity. As mentioned earlier, the catalyst activity was measured by manually monitoring the flow meter controller reading. As the measuring could only be carried out during working hours, the measurement data is incomplete and thus not perfectly accurate. However, the experiments show well the general trend, how the catalysts behave under longer experiments.

8.2 Product analysis

Some errors affecting the results also occur in the analysis of the gaseous and liquid products. When analyzing the gaseous products, two analyzes were run on every sample and the average of the results was taken. The amount of methane was generally consistent between the two runs, but the amount of carbon dioxide varied. In addition, no correlation was found between the amount of carbon dioxide and other parameters. This variation is most likely due to the air in the samples. Some amount of air was always found in the gas samples and the carbon dioxide in the air then skews the results, making them unreliable. The air has probably

gotten in to the sample either during the sampling of the product gas, or when the gas is fed to the GC for analysis.

For the liquid products, only one analysis run was carried out and some fluctuations in the analysis results are expected as well, causing slight errors in the results. Highest error in the analysis of the liquid products is in the determination of decomposition product composition. The isolated mass spectrum peaks were generally small, making it possible that some peaks were not detected by the GC-MS. In addition, accurate integration of the peaks proved to be difficult, causing even more error to the results.

8.3 Deviation of the results

Three experiments with similar conditions (T = 300 °C, and WHSV = 4.57 h^{-1}) were carried out on the Pt/Al_2O_3 catalysts and two on the Pt/TiO_2 catalyst to observe possible deviation in the results caused by catalyst deactivation or other factors, and to analyze the replicability of the experiments. In Tables 8-10, the hydrogen flow rate and degree of dehydrogenation obtained in these experiments are presented together with their averages and deviations from these averages.

Table 8. Deviation of results in Pt/Al_2O_3 packed bed experiments at T = 300 °C, and WHSV = 4.57 h^{-1}

experiment	hydrogen flow (ml/min)	deviation	dodh	deviation
1st	(26.63)	-	(45.48 %)	-
2nd	18.44	1.27 %	30.91 %	1.50 %
3rd	18.91	1.27 %	31.85 %	1.50 %
average	18.67		31.38 %	

Table 9. Deviation of results in Pt/Al_2O_3 washcoat experiments at T = 300 °C, and WHSV = 4.57 h^{-1}

experiment	hydrogen flow (ml/min)	deviation	dodh	deviation
1st	(21.85)		(30.80 %)	
2nd	19.86	2.44 %	28.54 %	2.30 %
3rd	18.91	2.44 %	27.26 %	2.30 %
average	19.38		27.90 %	

Table 10. Deviation of results in Pt/TiO_2 washcoat experiments at T = 300 °C, and WHSV = 4.57 h^{-1}

experiment	hydrogen flow (ml/min)	deviation	dodh	deviation
1st	(13.70)	8.24 %	(45.95 %)	8.03 %
2nd	11.61	8.24 %	39.12 %	8.03 %
average	12.65		42.54 %	

As can be seen from the Table 8, the first Pt/Al_2O_3 packed bed experiments differs distinctively from the others. Thus, in order to minimize the error in the results, the average of the two latter experiments were used. For the Pt/Al_2O_3 washcoat catalyst the first result also differs from the others (Table 9), albeit not as much as for the Pt/Al_2O_3 packed bed, and the average of the two latter experiments' results were used for the washcoated Pt/Al_2O_3 as well. The higher activity of the catalyst in the first experiments is most likely due to the fresh catalyst being more active and then deactivating slightly. For the Pt/TiO_2 washcoat, also the results from the latter experiment were used because it represents the more realistic situation where the catalyst is not fresh.

9. Conclusions

The dehydrogenation of H18-dibenzyltoluene over different platinum catalysts was studied in this thesis. In the literature part of the thesis, different LOHC compounds and reactor concepts for LOHC dehydrogenation were reviewed and compared. The aim of the experimental part was to study platinum catalyst with different supports to find the most suitable catalyst for H18-DBT dehydrogenation.

The most promising reactor concepts for commercial LOHC dehydrogenation applications are heat exchanger reactors, metallic monolith reactors and other micro-structured reactors. They offer the best mass and heat transfer properties of all studied reactor concepts and thus are prime candidates for commercial applications. However, these concepts lack technical maturity, meaning that research still needs to be carried out before these reactors can be utilized efficiently in larger scale commercial applications.

The catalysts studied for this thesis were Pt/Al_2O_3 in packed bed and washcoat form, Pt/TiO_2 in washcoat form and Pt/C as a packed bed. Of the catalysts tested, Pt/TiO_2 was found to be the most suitable catalyst for H18-DBT dehydrogenation as it generally yielded the highest degree of dehydrogenation and lowest degree of decomposition. The experiments on Pt/C catalyst were unsuccessful due to the rapid deactivation of the catalyst. This was likely caused by faulty catalyst preparation. However, the results obtained from the other experiments were well in line with literature, with the exception of the degrees of decomposition, which were significantly higher in the experiments performed for this thesis. A few causes of results affecting errors were noted during the experimental work, most notably the effect of varying room temperature on the hydrogen flow. In addition, errors are inherent in the analysis of the products and decomposition products, for example, the carbon dioxide in the air caused the amount of carbon dioxide in the gas samples to be unmeasurable. Nevertheless, observations considering the gas decomposition products could be made from the amount of methane in the gas samples.

When comparing packed bed and washcoat catalysts in small scale experiments, they performed similarly. However, when scaled up, the packed bed is expected to

yield higher conversion due to better reactant/catalyst contact. Yet, the packed bed also yields significantly higher degree of decomposition. Because of this, even though packed bed catalysts could possibly perform better in larger scale, washcoat catalysts are more suitable for commercial applications, where the recyclability of the LOHC compounds are vital. However, the application of the washcoat reactors is more difficult because, when the catalyst deactivates, the whole reactor must be changed whereas in packed bed reactors only the catalyst can be changed. This poses a reactor design challenge for the commercial applications.

Based on the literature review and the experimental results, a washcoated Pt/TiO_2 catalyst in a micro-structured (monolith) or a multitube heat exchanger reactor is a promising reactor and catalyst configuration for commercial applications. Washcoated Pt/TiO_2 offers the best degree of dehydrogenation and degree of decomposition at typical dehydrogenation conditions. However, washcoated catalysts require low diameter tubular reactors for efficient mass transfer. Thus, tubular micro-structured reactors or heat exchanger reactors with multiple narrow tubes are the best reactor types for washcoated catalysts.

Further research still needs to be carried out on LOHC dehydrogenation. The next step should be to test this concept in a larger scale to see if the proposed configuration would work in practice and to optimize the reactor design. Other important studies would be to test the activity and stability of the catalyst during longer periods of continuous operation to truly determine how the catalyst behaves under long periods of operation. In addition, more accurate catalyst characterization should be carried out to further improve and optimize the dehydrogenation catalysts.

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APPENDIX 1

Table 1. List of all experiments.

Experiment	**Catalyst**	**Temperature °C**	**LHSV h^{-1}**	**WHSV h^{-1}**	**Testing the effect of**
1-1	Pt/Al_2O_3 part.	300	3	4.57	Flow rate
1-2	Pt/Al_2O_3 part.	300	2	3.05	Flow rate
1-3	Pt/Al_2O_3 part.	300	1	1.52	Flow rate
1-4	Pt/Al_2O_3 part.	300	3	4.57	Temperature
1-5	Pt/Al_2O_3 part.	280	3	4.57	Temperature
1-6	Pt/Al_2O_3 part.	290	3	4.57	Temperature
1-7	Pt/Al_2O_3 part.	270	3	4.57	Temperature
1-8	Pt/Al_2O_3 part.	300	3	4.57	Temperature
1-9	Pt/Al_2O_3 part.	300	3	4.57	Long operation
2-1	Pt/Al_2O_3 wc.	300	3	4.5	Flow rate
2-1	Pt/Al_2O_3 wc.	300	2	3	Flow rate
2-3	Pt/Al_2O_3 wc.	300	1	1.5	Flow rate
2-4	Pt/Al_2O_3 wc.	300	3	4.5	Temperature
2-5	Pt/Al_2O_3 wc.	280	3	4.5	Temperature
2-6	Pt/Al_2O_3 wc.	290	3	4.5	Temperature
2-7	Pt/Al_2O_3 wc.	270	3	4.5	Temperature
2-8	Pt/Al_2O_3 wc.	300	3	4.5	Temperature
2-9	Pt/Al_2O_3 wc.	300	3	4.5	Long operation
3-1	Pt/C part.	300	3	4.5	Flow rate
4-1	Pt/TiO_2 wc.	300	3	4.5	Temperature
4-2	Pt/TiO_2 wc.	280	3	4.5	Temperature
4-3	Pt/TiO_2 wc.	290	3	4.5	Temperature
4-4	Pt/TiO_2 wc.	270	3	4.5	Temperature
4-5	Pt/TiO_2 wc.	300	3	4.5	Temperature
4-6	Pt/TiO_2 wc.	300	3	4.5	Long operation

APPENDIX 2

An example of GC-MS chromatogram is presented in Figure 1.

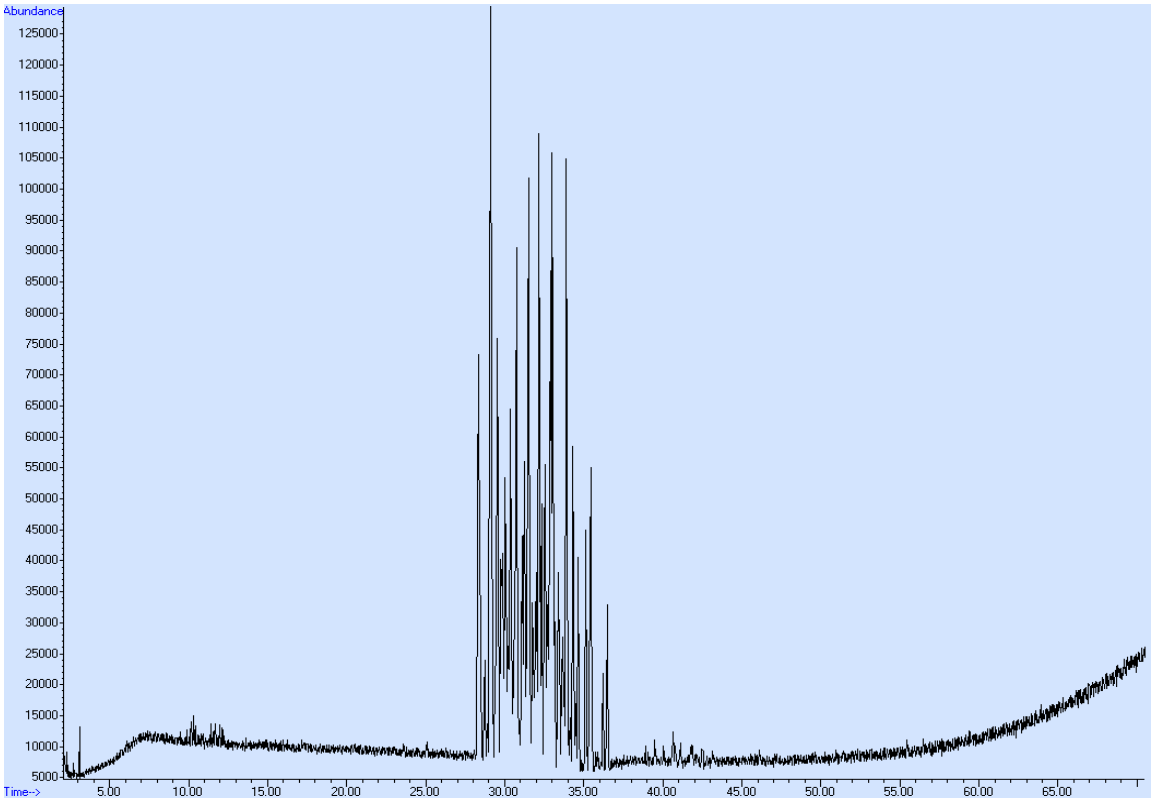

Figure 1. GC-MS chromatogram obtained from liquid product analysis.

APPENDIX 3

The mass spectra of H18-DBT used as a reactant is presented in Figures 1-3. In Figure 1, the mass spectra of products with different degrees of hydrogenation (H18-DBT and H12-DBT) is presented. In Figure 2, the mass spectra of one-ringed decomposition products, benzene and methylcyclohexane, is presented. In Figure 3, the mass spectra of two-ringed decomposition product, H12-benzyltoluene, is presented. Other common decomposition products, such as toluene or two ringed compounds with methyl groups, were not detected in the reactant mixture.

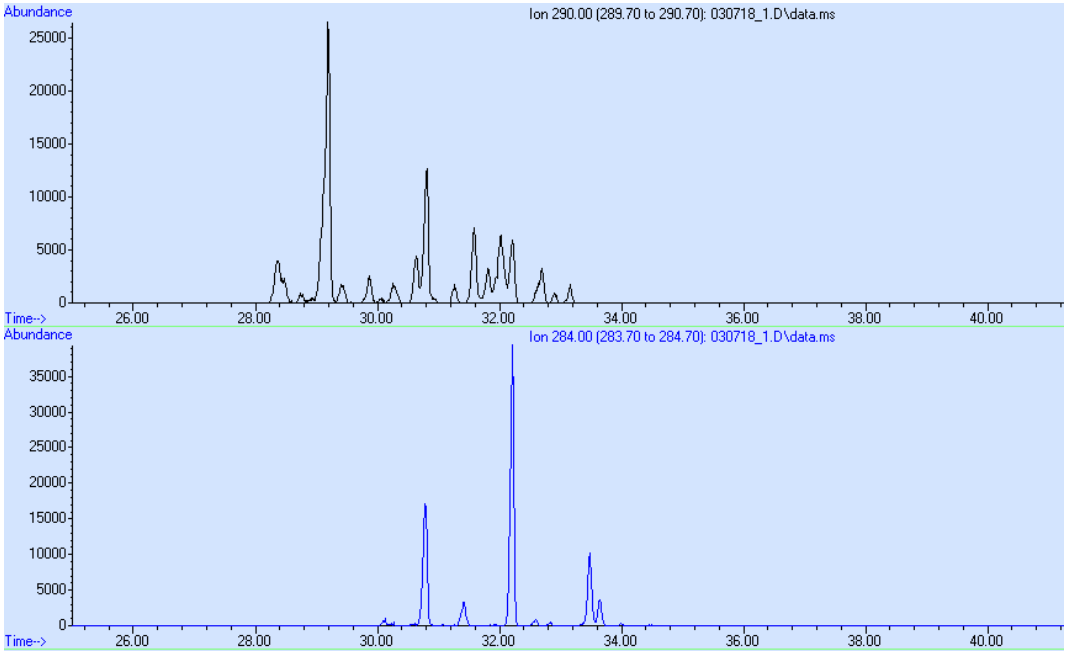

Figure 1. Mass spectra of H18-DBT (m/z = 290) and H12-DBT (m/z = 284).

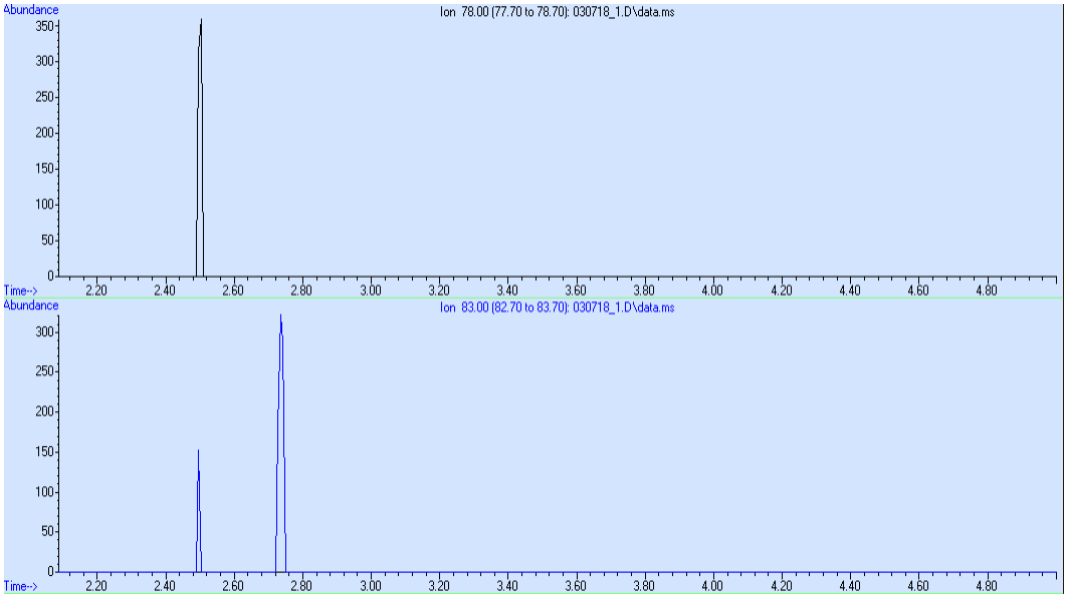

Figure 2. Mass spectra of one ringed decomposition product, benzene (m/z = 78) and methylcyclohexane (m/z = 83).

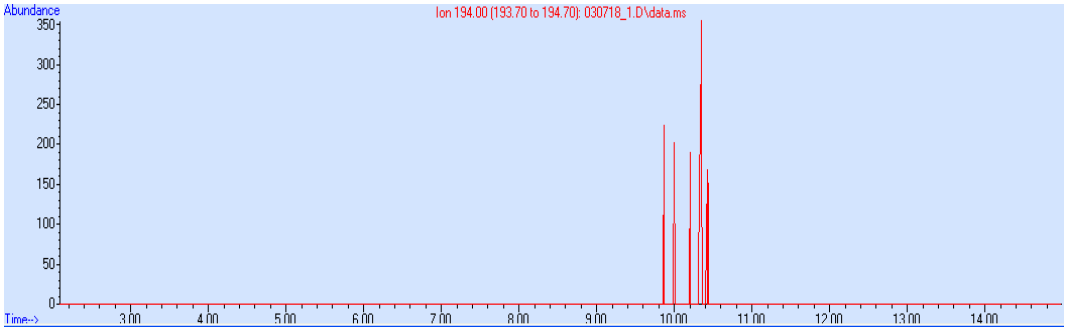

Figure 3. Mass spectra of two ringed decomposition product H12-benzyltoluene (m/z = 194).

The areas of the H18-DBT and H12-DBT mass spectra are presented in Table 1. The areas of decomposition products mass spectra are presented in Table 2.

Table 1. Areas of H18-DBT and H12-DBT mass spectra

Molecule	Area
H18-DBT	4902127
H12-DBT	3107487
H6-DBT	0
H0-DBT	0
Total	8009614

Table 2. Areas of decomposition products mass spectra

One ringed		**Two ringed**	
Molecule	Area	Molecule	Area
Benzene	2660	H12	7730,18
MCH	3972,75	H6	0
Toluene	0	H0	0
Total	6632,75	Total	7730,18
Total area of decomposition products			14362,93

From the mass spectra areas, the degree of decomposition can be calculated with equation 10.

$$Degree\ of\ decomposition\ (\%) = \frac{A_{dec}}{A_{total}} \cdot 100\% = \frac{14362{,}93}{14362{,}93 + 8009614} \cdot 100\%$$

$$Degree\ of\ decomposition\ = 0{,}178\ \%$$

APPENDIX 4

The ^{1}H-NMR spectra of H0-DBT, H18-DBT and product from experiment 1-2 (see Appendix 1) are presented in Figure 1. The determination of the degree of dehydrogenation from the NMR spectra is presented by Do et al. [76]

Figure 1. ^{1}H-NMR spectra of H0-DBT, H18-DBT and product from experiment 1-2.